The Design of a Photoredox Catalyst that Enables the Direct Synthesis of Carbamate-Protected Primary Amines via Photoinduced, Copper-Catalyzed N-Alkylation Reactions of Unactivated Secondary Halides

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Supporting Information

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I. General Information

Unless otherwise noted, materials were either purchased from commercial suppliers and used as received or prepared via literature procedures. Ligand **L1** was synthesized according to a literature procedure[1] and recrystallized from a cold, saturated solution in Et_2O/MeCN. Solvents were deoxygenated and dried by thoroughly sparging with argon followed by passage through an activated column in a solvent purification system.

All manipulations of air-sensitive materials were carried out in oven-dried glassware using standard Schlenk or glovebox techniques under an N_2 atmosphere. Silicycle *Silia*Flash® P60 silica gel (particle size 40–63 μm) was used for flash chromatography. Analytical thin layer chromatography was conducted with glass TLC plates (silica gel 60 F254), and spots were visualized under UV light or after treatment with standard TLC stains.

X-band EPR measurements were made with a Bruker EMX spectrometer at 77 K. Simulation of EPR data was conducted using the software EasySpin.[2]

IR measurements were recorded on a Bruker ALPHA Diamond ATR or using a Perkin Elmer Paragon 1000 spectrometer using thin films deposited on KBr plates.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Ascend 400 MHz, a Varian 300 MHz, a Varian 400 MHz, a Varian 500 MHz, or a Varian 600 MHz spectrometer with $CHCl_3$ (^{1}H, δ = 7.26) and $CDCl_3$ (^{13}C, δ = 77.0) as internal references and with 85% H_3PO_4 (^{31}P) as an external reference. Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent). GC analyses were carried out on an Agilent 6890 Series system with an HP-5 column (length 30 m, I.D. 0.25 mm).

X-ray crystallography studies were carried out at the Beckman Institute Crystallography Facility on a Bruker D8 Venture kappa duo photon 100 CMOS instrument (Mo Kα radiation). Structures were solved using SHELXT and refined against F^2 by full-matrix least squares with SHELXL and OLEX2. Hydrogen atoms were added at calculated positions and refined using a riding model. The crystals were mounted on a glass fiber or a nylon loop with Paratone N oil.

Steady-state fluorimetry was performed in the Beckman Institute Laser Resource Center (BILRC; California Institute of Technology). Steady-state emission spectra were collected on a Jobin S4 Yvon Spec Fluorolog-3-11 with a Hamamatsu R928P photomultiplier tube detector with photon counting. Absorbance spectra were acquired on a Cary 50 UV-Vis spectrophotometer with a Unisoku Scientific Instruments cryostat to maintain temperature.

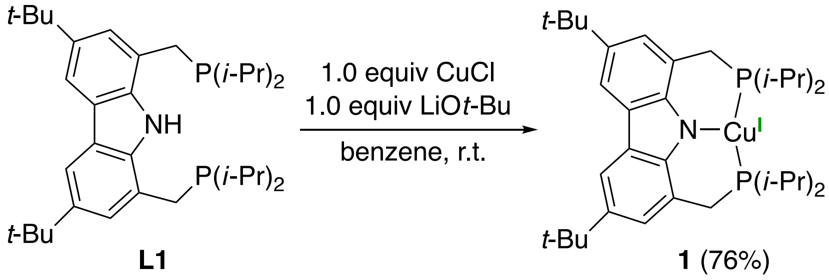
Electrochemical measurements were carried out in a thick-walled one-component electrochemical cell fitted with a Teflon stopcock and tungsten leads protruding from the top of the apparatus in a nitrogen-filled glovebox. A CH Instruments 600B electrochemical analyzer or a CHS-3600B potentiostat was used for data collection. A freshly-polished glassy carbon electrode was used as the working electrode, and platinum wire was used as the auxiliary electrode. Solutions (THF) of electrolyte (0.1 M tetra-*n*-butylammonium hexafluorophosphate) contained ferrocene (~1 mM, post measurement), to serve as an internal reference, and analyte (~1 mM).

Mass spectral data were collected on a Thermo LCQ or LTQ ion trap mass spectrometer, or on an Agilent 5973 mass spectrometer.

Photolytic reactions were performed using 34 W Kessil H150 Blue LED lamps, a 100 W Blak-Ray Long Wave Ultraviolet Lamp (Hg), a 100-W Blak-Ray B-100Y High Intensity Inspection Lamp (Hg), or a Luzchem LZC-4V photoreactor equipped with LZC-UVC lamps centered at 254 nm, LZC-UVA lamps centered at 350 nm, or LZC-420 lamps centered at 420 nm. If required, the temperature was maintained with an isopropanol bath cooled by an SP Scientific cryostat.

Elemental analyses were performed by Midwest Microlab (Indianapolis, IN).

II. Preparation and Characterization of Copper Complex 1



Complex 1 (eq 3). 3,6-Di-*tert*-butyl-1,8-bis((diisopropylphosphanyl)methyl)-9*H*-carbazole (**L1**) (310 mg, 0.57 mmol, 1.0 equiv), CuCl (55 mg, 0.56 mmol, 1.0 equiv), LiO*t*-Bu (48 mg, 0.60 mmol, 1.0 equiv), a magnetic stir bar, and dry, degassed benzene (10 mL) were added to a 20 mL scintillation vial. The mixture was vigorously stirred overnight at room temperature. Next, the mixture was filtered through a pad of Celite, and the filtrate was concentrated in vacuo. The ^1H NMR spectrum of the residue showed the clean formation of the target compound, which can be further purified by recrystallization from a mixture of benzene/*n*-hexanes at –35 °C to afford colorless crystals (260 mg, 76% yield). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a concentrated sample in Et_2O at room temperature.

^1H NMR (400 MHz, C_6D_6) δ 8.49 (s, 2H), 7.39 (s, 2H), 3.19 (s, 4H), 1.65 (s, 18H), 1.63–1.57 (m, 4H), 0.89 (dq, J = 26.9, 7.1 Hz, 24H).

^{13}C NMR (101 MHz, C_6D_6) δ 148.0, 137.5, 125.5, 123.1, 119.8, 115.7, 34.8, 32.8, 26.4 (t, J = 8.8 Hz, 23.1 (t, J = 7.4 Hz), 19.7 (t, J = 3.8 Hz), 18.8 (t, J = 2.0 Hz).

^{31}P NMR (162 MHz, C_6D_6) δ 21.78.

Anal. Calcd for $C_{34}H_{54}CuNP_2$: C, 67.80; H, 9.04; N, 2.33. Found: C, 68.16; H, 9.38; N, 2.22.

Figure S1. Excitation and emission spectra of a solution of copper complex **1** in THF.

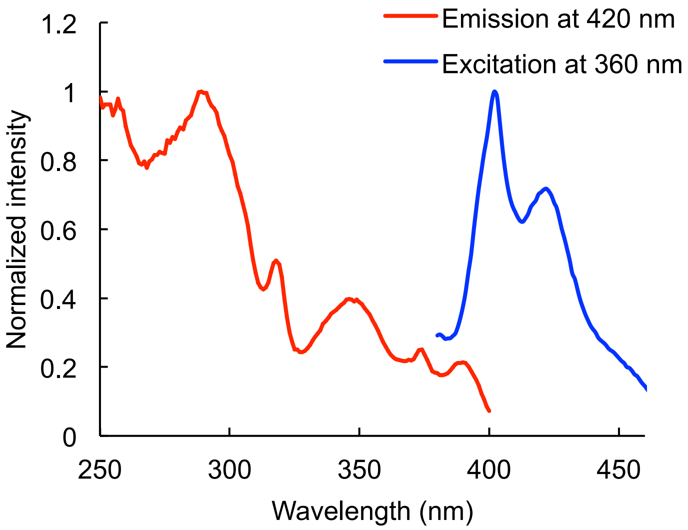
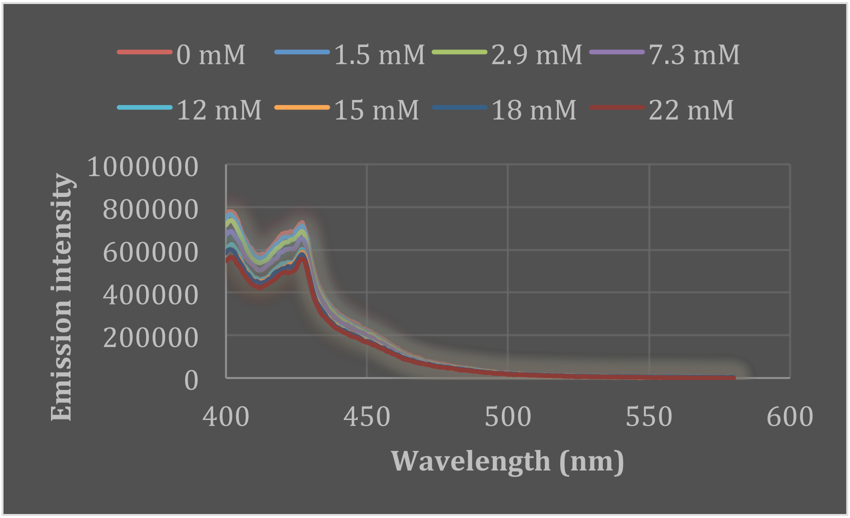
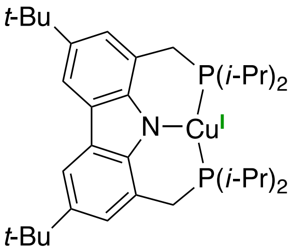
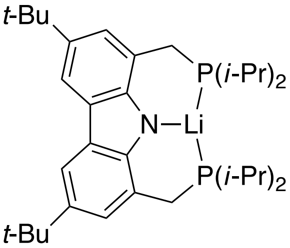


Figure S2. The emission spectra of a solution of copper complex **1** in THF upon irradiation at 380 nm in the presence of varying amounts of 2-bromo-4-phenylbutane.

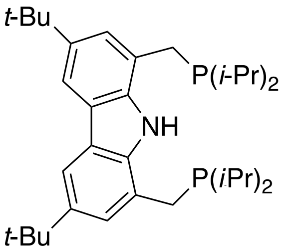




1



LiPNP



L1

Figure S3. UV-vis spectra in THF at room temperature.

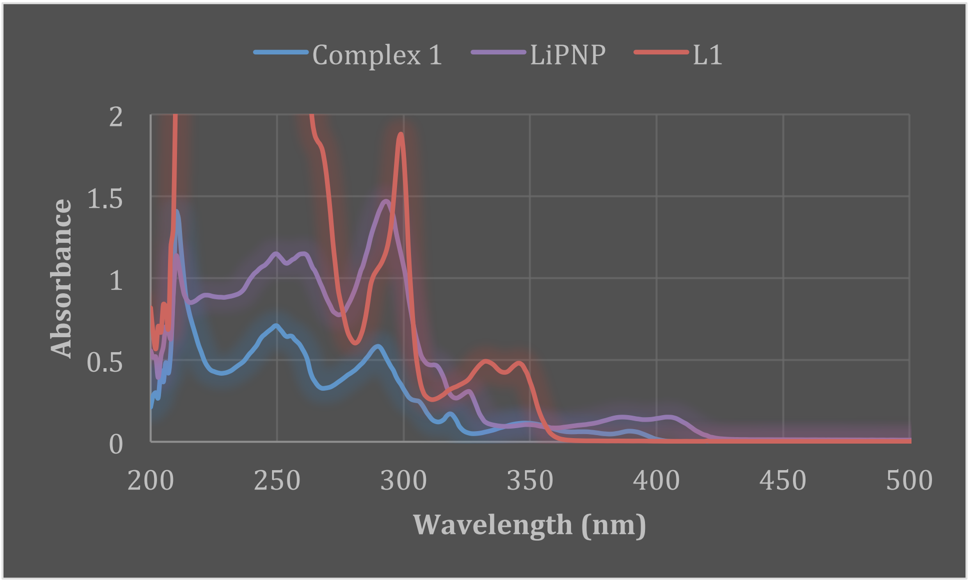
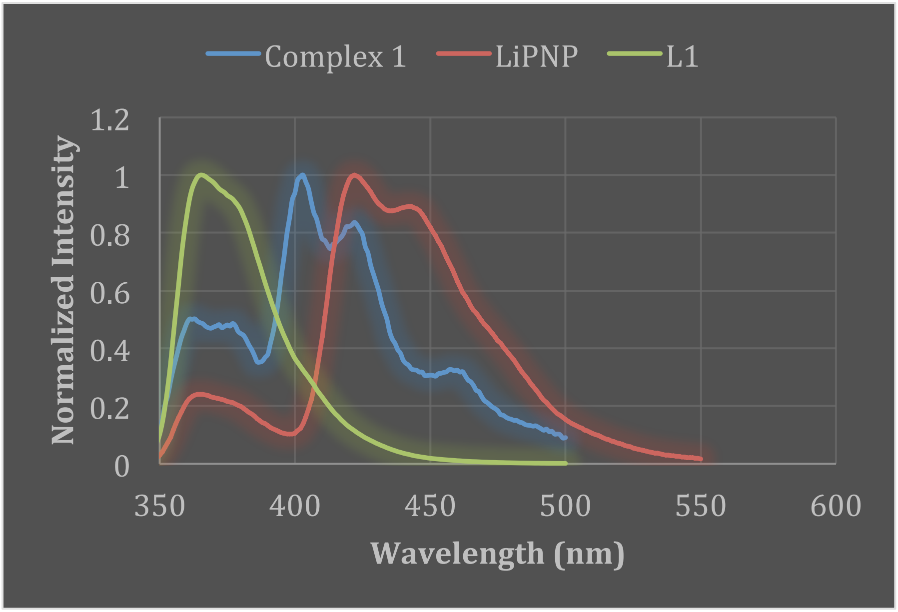


Figure S4. Emission spectra in THF at room temperature (excitation at 300 nm).



III. Photoinduced, Copper-Catalyzed Alkylations

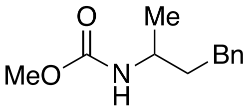
Preparation of a reaction mixture on a Schlenk line (liquid electrophiles). CuBr, ligand **L1**, LiO*t*-Bu, and the carbamate were added to an 8 mL borosilicate glass vial that contained a magnetic stir bar. The vial was capped with a PTFE-lined septum cap, and then it was evacuated and backfilled with nitrogen (3 cycles). Next, DME and the electrophile were added in sequence via syringe, and the mixture was stirred at room temperature until the solids had dissolved (5 min). The vial was then detached from the Schlenk line.

Preparation of a reaction mixture on a Schlenk line (solid electrophiles). CuBr, ligand **L1**, LiO*t*-Bu, the carbamate, and the electrophile were added to an 8 mL borosilicate glass vial that contained a magnetic stir bar. The vial was capped with a PTFE-lined septum cap, and then it was evacuated and backfilled with nitrogen (3 cycles). Next, DME was added via syringe, and the mixture was stirred at room temperature until the solids had dissolved (5 min). The vial was then detached from the Schlenk line.

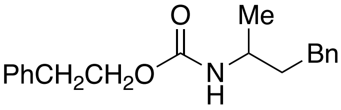
Note: We recommend that CuBr (white or off-white solid) and LiO*t*-Bu (hygroscopic) be stored in a glovebox. Solutions of $BocNH_2$ and LiO*t*-Bu in DME can be prepared under nitrogen, stirred for 10 min, and filtered through a PTFE syringe filter to remove impurities.

General Procedure: Irradiation of the reaction mixture with blue LED lamps. The reaction vial and a magnetic stir bar were submerged in a low-form hemispherical Dewar flask filled with water in a well-ventilated fume hood. Three 34-watt blue-LED lamps were placed 3” from the vial (as close to the vial as possible, without the lamps being in contact with water), and the vial was irradiated for 16 h. The temperature of the water bath was maintained below 30 °C with a table fan. A typical setup is shown above.

Workup. After irradiation, the reaction mixture was diluted with EtOAc (5 mL) and then washed with aqueous NH_4Cl (5 mL). The aqueous layer was extracted with EtOAc (5 mL x 3), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel.



Methyl (4-phenylbutan-2-yl)carbamate. Table 2, entry 1 [129830-34-8]. The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), methyl carbamate (158 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→30% Et_2O/hexanes). Colorless oil. First run: 131 mg (90%). Second run: 132 mg (91%).



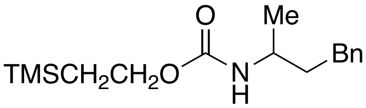
Phenethyl (4-phenylbutan-2-yl)carbamate. Table 2, entry 2. The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), phenethyl carbamate (347 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→40% Et_2O/hexanes). White solid. First run: 140 mg (67%). Second run: 141 mg (68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 4H), 7.23–7.16 (m, 6H), 4.57 (d, *J* = 7.0 Hz, 1H), 4.29 (t, *J* = 7.0 Hz, 2H), 3.79–3.72 (m, 1H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.70–2.58 (m, 2H), 1.73 (q, *J* = 6.6 Hz, 2H), 1.16 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 141.8, 138.1, 129.0, 128.51, 128.47, 128.4, 126.5, 125.9, 65.1, 46.9, 39.0, 35.6, 32.5, 21.4.

FT-IR (film): 3322, 2965, 1682, 1548, 1454, 1267, 1111, 699 cm^{-1}.

MS (ESI) m/z $(M+Na)^+$ calcd for $C_{19}H_{23}NO_2Na$: 320.2, found: 320.2.



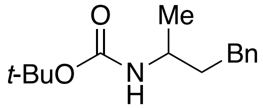
2-(Trimethylsilyl)ethyl (4-phenylbutan-2-yl)carbamate. Table 2, entry 3. The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), 2-(trimethylsilyl)ethyl carbamate (339 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→30% Et_2O/hexanes). Colorless oil. First run: 161 mg (78%). Second run: 153 mg (74%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.26 (m, 2H), 7.19–7.17 (m, 3H), 4.50 (br, 1H), 4.20–4.09 (m, 2H), 3.77 (br, 1H), 2.72–2.60 (m, 2H), 1.74 (q, *J* = 7.1 Hz, 2H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.01–0.97 (m, 2H), 0.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 141.9, 128.5, 128.4, 126.0, 62.9, 46.9, 39.2, 32.6, 21.5, 17.9, –1.4.

FT-IR (film): 3326, 2953, 1691, 1534, 1250, 1057, 837, 698 cm^{-1}.

MS (EI) m/z $(M+H)^+$ calcd for $C_{16}H_{28}NO_2Si$: 294.1, found: 294.0.



***tert*-Butyl (4-phenylbutan-2-yl)carbamate. Table 2, entry 4 [1206464-59-6].** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), $BocNH_2$ (246 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→35% Et_2O/hexanes). White solid. First run: 150 mg (86%). Second run: 153 mg (88%).

As indicated in eq 1, the title compound was also prepared according to a literature procedure,[3] using CuI (19.5 mg, 0.10 mmol), LiO*t*-Bu (160 mg, 2.0 mmol), $BocNH_2$ (117 mg, 1.0 mmol), and 2-bromo-4-phenylbutane (426 mg, 2.0 mmol) in a mixture of DMF (0.8 mL) and MeCN (5.4 mL). Purification by column chromatography (10%→35% Et_2O/hexanes) afforded a pale-yellow solid. First run: 110 mg (44%). Second run: 106 mg (43%).

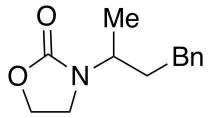
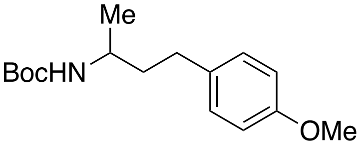


Table 2, entry 5 [1542235-59-5]. The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), 2-oxazolidinone (183 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (70%→90% Et_2O/hexanes). Pale-yellow oil. First run: 117 mg (76%). Second run: 112 mg (73%).



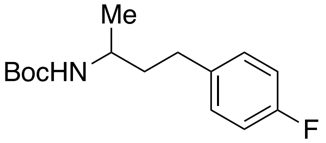
***tert*-Butyl (4-(4-methoxyphenyl)butan-2-yl)carbamate. Table 3, entry 1.** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), $BocNH_2$ (246 mg, 2.1 mmol), and 1-(3-bromobutyl)-4-methoxybenzene (170 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (15%→35% Et_2O/hexanes). White solid. First run: 160 mg (82%). Second run: 156 mg (80%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.32 (br, 1H), 3.78 (s, 3H), 3.69 (br, 1H), 2.74–2.45 (m, 2H), 1.79–1.58 (m, 2H), 1.45 (s, 9H), 1.15 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 155.4, 134.0, 129.3, 113.9, 79.0, 55.3, 46.4, 39.5, 31.6, 28.5, 21.5.

FT-IR (film): 3353, 2974, 1688, 1612, 1514, 1246, 1175, 1061 cm^{-1}.

MS (ESI) m/z $(M+Na)^+$ calcd for $C_{16}H_{25}NO_3Na$: 302.2, found: 302.1.



***tert*-Butyl (4-(4-fluorophenyl)butan-2-yl)carbamate. Table 3, entry 2.** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), $BocNH_2$ (246 mg, 2.1 mmol), and 1-(3-bromobutyl)-4-fluorobenzene (162 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→35% Et_2O/hexanes). White solid. First run: 135 mg (72%). Second run: 130 mg (69%).

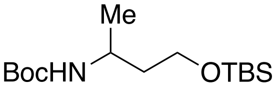
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.95 (t, *J* = 8.8 Hz, 2H), 4.32 (s, 1H), 3.69 (s, 1H), 2.62 (dd, *J* = 9.6, 6.4 Hz, 2H), 1.77–1.62 (m, 2H), 1.45 (s, 9H), 1.15 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 161.2 (d, *J* = 243.2 Hz), 155.4, 137.5, 129.7 (d, *J* = 7.8 Hz), 115.1 (d, *J* = 21.0 Hz), 79.0, 46.2, 39.3, 31.7, 28.5, 21.4.

^{19}F NMR (282 MHz, CDCl$_3$) δ –117.9.

FT-IR (film): 3342, 2976, 1690, 1601, 1511, 1455, 1366, 1223, 1174, 1060, 827 cm^{-1}.

MS (ESI) m/z (M+Na)$^+$ calcd for $C_{15}H_{22}FNO_2Na$: 290.2, found: 290.0.



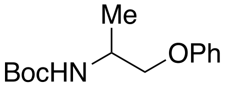
***tert*-Butyl (4-((*tert*-butyldimethylsilyl)oxy)butan-2-yl)carbamate. Table 3, entry 3.** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and 1 (3-bromobutoxy)(*tert*-butyl)dimethylsilane (187 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→30% Et$_2$O/hexanes). Colorless oil. First run: 157 mg (74%). Second run: 149 mg (70%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.12 (s, 1H), 3.80–3.69 (m, 2H), 3.66–3.61 (m, 1H), 1.69 (br, 1H), 1.57–1.51 (m, 1H), 1.39 (s, 9H), 1.12 (d, *J* = 6.6 Hz, 3H), 0.86 (s, 9H), 0.02 (s, 6H).

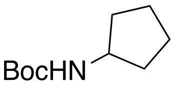
^{13}C NMR (101 MHz, CDCl$_3$) δ 155.5, 78.6, 60.5, 45.2, 38.6, 28.5, 26.0, 20.9, 18.2, –5.4.

FT-IR (film): 3350, 2931, 1704, 1506, 1365, 1253, 1177, 1094, 836, 777 cm^{-1}.

MS (ESI) m/z (M+Na)$^+$ calcd for $C_{15}H_{33}NO_3SiNa$: 326.2, found: 326.1.

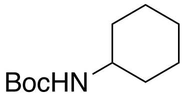


***tert*-Butyl (1-phenoxypropan-2-yl)carbamate. Table 3, entry 4 [1824064-92-7].** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and (2-bromopropoxy)benzene (151 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→30% Et$_2$O/hexanes). White solid. First run: 103 mg (59%). Second run: 93 mg (53%).

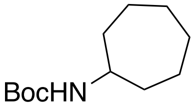


***tert*-Butyl cyclopentylcarbamate. Table 3, entry 5 [153789-22-1].** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and bromocyclopentane (104 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→30% Et$_2$O/hexanes). White solid. First run: 65 mg (50%). Second run: 63 mg (49%).

Irradiation under 100-watt Hg lamp: First run: 95 mg (73%). Second run: 98 mg (76%).



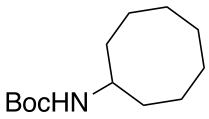
***tert*-Butyl cyclohexylcarbamate. Table 3, entry 6 [3712-40-1].** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and bromocyclohexane (114 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→20% Et$_2$O/hexanes). White solid. First run: 110 mg (79%). Second run: 116 mg (83%).



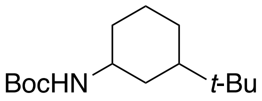
***tert*-Butyl cycloheptylcarbamate. Table 3, entry 7 [1005795-57-2].** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 0.21 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and bromocycloheptane (124 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→30% Et$_2$O/hexanes). White solid. First run: 131 mg (88%). Second run: 131 mg (88%).

Procedure for gram-scale reaction. A 100 mL Schlenk flask was charged with CuBr (120 mg, 0.84 mmol), ligand **L1** (114 mg, 0.21 mmol), LiO*t*-Bu (1.7 g, 21 mmol), BocNH$_2$ (2.5 g, 21 mmol), and a magnetic stir bar. The Teflon plug valve was sealed with a rubber septum, and the vessel was evacuated and backfilled with N$_2$ (3 cycles). DME (80 mL) was added via syringe, and then the mixture was stirred at room temperature for 5 min. Next, the electrophile (7.0 mmol) was added in one portion via syringe. The rubber septum was quickly replaced under a positive flow of N$_2$ with a Teflon screw cap. The vessel was sealed and placed in a low-form hemispherical Dewar flask filled with water. Four 34-watt blue-LED lamps were placed 2" from the flask, which was irradiated for 72 h. The temperature of the water bath was controlled by a standard table fan. Water was refilled occasionally to prevent warming of the reaction mixture. The Schlenk flask was periodically shaken vigorously to provide even mixing of the material. After 72 h, the reaction mixture was diluted with EtOAc (75 mL) and washed with aqueous NH$_4$Cl (50 mL). The aqueous layer was extracted with EtOAc (50 mL x 3), and the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel.

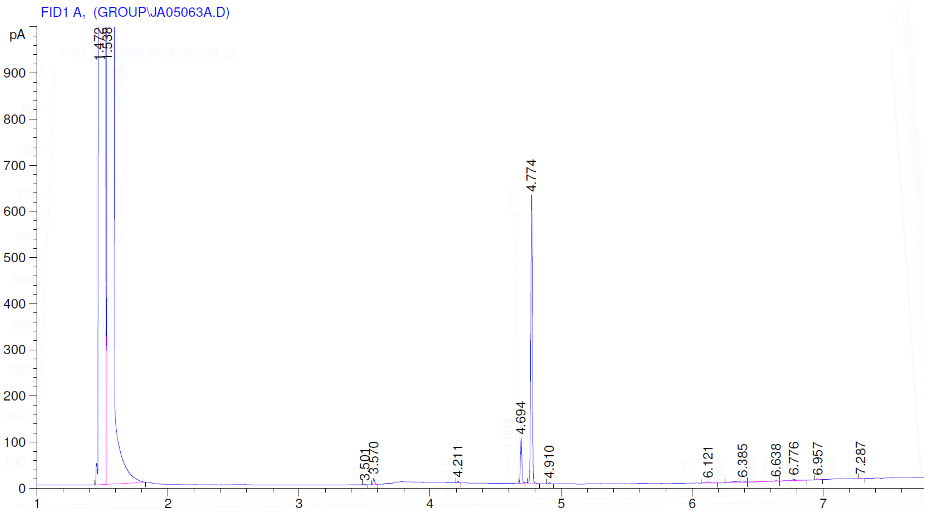
The title compound was prepared according to the procedure for gram-scale reactions, using bromocycloheptane (1.24 g, 7.0 mmol), and purified by column chromatography (10%→30% Et$_2$O/hexanes). Pale-yellow solid. First run: 990 mg (66%). Second run: 994 mg (67%). Unreacted bromocycloheptane was recovered by additional purification by flash column chromatography, eluting with hexanes. The combined fractions were concentrated in vacuo with cooling, to minimize the loss of bromocycloheptane. First run: 290 mg (23%). Second run: 270 mg (22%).



***tert*-Butyl cyclooctylcarbamate. Table 3, entry 8 [544478-04-8].** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), $BocNH_2$ (246 mg, 2.1 mmol), and bromocyclooctane (134 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→30% Et_2O/hexanes). Pale-yellow solid. First run: 130 mg (82%). Second run: 126 mg (79%).



***tert*-Butyl (3-(*tert*-butyl)cyclohexyl)carbamate. Table 3, entry 9.** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), $BocNH_2$ (246 mg, 2.1 mmol), and 1-bromo-3-(*tert*-butyl)cyclohexane (153 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (7%→35% Et_2O/hexanes) as a mixture of diastereomers. The relative stereochemistry was determined based on the chemical shifts of the diagnostic methine protons (3.4 ppm = axial = cis isomer; 3.9 ppm = equatorial = trans isomer). Pale-yellow oil. First run: 151 mg (84%), 6.7:1 dr. Second run: 155 mg (87%), 6.4:1 dr. A representative GC trace is shown below (product peaks are at 4.774 and 4.694 min).

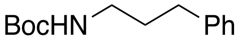


^{1}H NMR (400 MHz, CDCl$_3$) δ 4.44 (br, 1H), 3.36 (br, 1H), 2.00–1.81 (m, 2H), 1.77–1.61 (m, 2H), 1.39 (s, 9H), 1.26–1.17 (m, 1H), 1.08–1.02 (m, 1H), 0.93–0.83 (m, 2H), 0.78 (s, 9H), 0.76–0.66 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 155.2, 78.9, 50.4, 47.1, 35.1, 33.8, 32.4, 28.5, 27.6, 26.5, 25.2.

FT-IR (film): 3337, 2942, 1687, 1504, 1366, 1314, 1173, 1047, 734 cm^{-1}.

MS (EI) m/z (M)$^+$ calcd for $C_{15}H_{29}NO_2$: 255.2, found: 255.1.

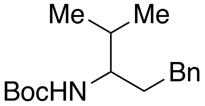


***tert*-Butyl (3-phenylpropyl)carbamate. [147410-39-7].** The title compound was synthesized according to the General Procedure, using a 100-watt Hg lamp, CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and (3-bromopropyl)benzene (139 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (10%→30% Et$_2$O/hexanes). Colorless oil. First run: 135 mg (82%). Second run: 130 mg (79%). In the absence of irradiation, no coupling is observed.

General Procedure 2:

Preparation of a reaction mixture in a nitrogen-filled glovebox. CuBr, ligand **L1**, LiO*t*-Bu, and the carbamate were added to an 8 mL borosilicate glass vial that contained a magnetic stir bar. Next, DME and the electrophile were added in sequence, the vial was capped with a PTFE-lined septum cap, and the mixture was stirred at room temperature until the solids had dissolved (5 min).

Irradiation of the reaction mixture with a Hg lamp; two-portion procedure. A low-form hemispherical Dewar flask was filled with isopropanol in a well-ventilated fume hood. A magnetic stir bar was added to the Dewar flask, and the isopropanol bath was cooled to –10 °C. The reaction vial was submerged in the isopropanol bath and allowed to cool for 5 min. A 100-watt Hg lamp was placed 4″ from the vial, and the vial was irradiated for 16 h. Then, the vial was transferred to a nitrogen-filled glovebox, and the reaction mixture was filtered through a PTFE-lined syringe filter into a new 8 mL vial that contained CuBr, ligand **L1**, LiO*t*-Bu, and the carbamate. The syringe filter was washed with a small amount of DME (0.1 mL). A magnetic stir bar was added to the vial, and the vial was capped and placed in the –10 °C bath. A 100-watt Hg lamp was placed 4″ away from the vial, and the sample was irradiated for an additional 24 h.



***tert*-Butyl (4-methyl-1-phenylpentan-3-yl)carbamate. Eq 5.** The title compound was synthesized according to General Procedure 2, using CuBr (7.5 mg x 2, 0.052 mmol x 2), ligand **L1**

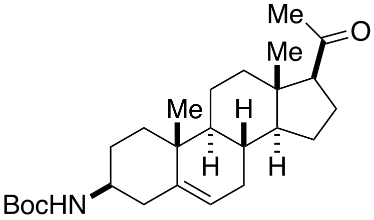
(13.5 mg x 2, 0.025 mmol x 2), LiO*t*-Bu (168 mg x 2, 2.1 mmol x 2), BocNH$_2$ (246 mg x 2, 2.1 mmol x 2), and (3-bromo-4-methylpentyl)benzene (168 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (5%→30% Et$_2$O/hexanes). Pale-yellow solid. First run: 128 mg (66%). Second run: 119 mg (61%).

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.30–7.27 (m, 2H), 7.20–7.17 (m, 3H), 4.33 (d, *J* = 10.4 Hz, 1H), 3.59–3.43 (m, 1H), 2.84–2.46 (m, 2H), 1.89–1.66 (m, 2H), 1.46 (s, 9H), 1.27–1.24 (m, 1H), 0.95–0.83 (m, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 156.1, 142.3, 128.43, 128.41, 125.8, 78.9, 55.5, 34.8, 32.9, 32.4, 28.5, 19.2, 17.7.

FT-IR (film): 3348, 2962, 1694, 1497, 1365, 1247, 1173, 1020, 869, 699 cm^{-1}.

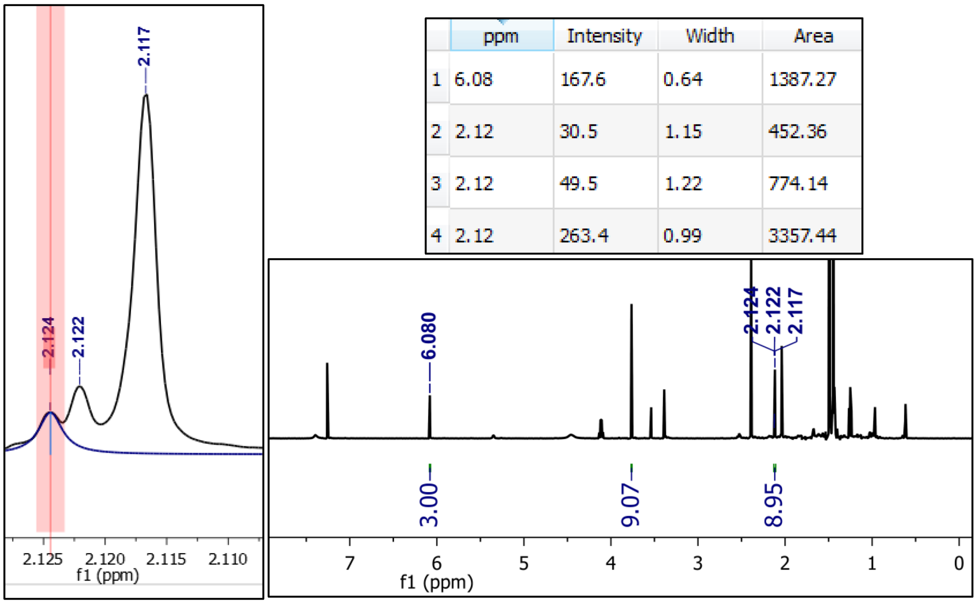
MS (ESI) m/z (M+Na)$^+$ calcd for $C_{17}H_{27}NO_2Na$: 300.2, found: 300.1.



***tert*-Butyl ((3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)carbamate. Eq 6.** The title compound was synthesized according to General Procedure 2 (except that the method for preparation of a reaction mixture on a Schlenk line for solid electrophiles was used), using CuBr (7.5 mg x 2, 0.052 mmol x 2), ligand **L1** (13.5 mg x 2, 0.025 mmol x 2), LiO*t*-Bu (168 mg x 2, 2.1 mmol x 2), BocNH$_2$ (246 mg x 2, 2.1 mmol x 2), and 1-((3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-bromo-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)ethan-1-one[4,5] (266 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (5%→30% Et$_2$O/hexanes). The major diastereomer was purified by column chromatography (15%→40% Et$_2$O/hexanes) and then recrystallization from cold Et$_2$O/hexanes. White solid. First run: 153 mg (53%; dr before purification: 4.3:1). Second run: 148 mg (51%; dr before purification: 4.6:1). A ^{1}H NMR spectrum of the unpurified mixture shows 90% conversion of the starting material to the C–N coupled products (Figure S5). Crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of a saturated solution in Et$_2$O/hexanes.

Essentially the same results were obtained when the materials were added in a single batch: The title compound was synthesized according to General Procedure 2 (except that the method for preparation of a reaction mixture on a Schlenk line for solid electrophiles was used), using CuBr (15 mg, 0.10 mmol), ligand **L1** (27 mg, 0.050 mmol), LiO*t*-Bu (340 mg, 4.2 mmol), BocNH$_2$ (490 mg, 4.2 mmol), and 1-((3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-bromo-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)ethan-1-one (266 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (5%→30% Et$_2$O/hexanes). 151 mg (52%). A ^{1}H NMR spectrum of the unpurified mixture shows 90% conversion of the starting material to the C–N coupled products.

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of the unpurified reaction mixture (pregnenolone-derived electrophile), showing 90% conversion to products (calibrated using 1,3,5-trimethoxybenzene). The relevant resonances are: 1) δ 6.080: 1,3,5-trimethoxybenzene; 2) δ 2.124: remaining starting material; 3) δ 2.122: minor diastereomer of product; 4) δ 2.117: major diastereomer of product.



	ppm	Intensity	Width	Area
1	6.08	167.6	0.64	1387.27
2	2.12	30.5	1.15	452.36
3	2.12	49.5	1.22	774.14
4	2.12	263.4	0.99	3357.44

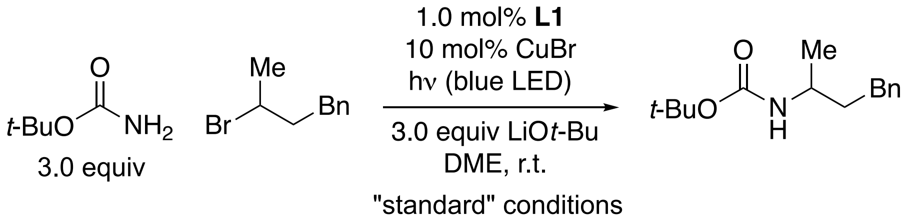
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39–5.33 (m, 1H), 4.40 (br, 1H), 3.36 (br, 1H), 2.53 (t, *J* = 8.9 Hz, 1H), 2.39–2.28 (m, 1H), 2.23–2.15 (m, 1H), 2.12 (s, 3H), 2.10–1.94 (m, 3H), 1.91–1.81 (m, 2H), 1.72–1.58 (m, 4H), 1.52–1.45 (m, 3H), 1.44 (s, 9H), 1.38–1.08 (m, 4H), 1.06–1.01 (m, 1H), 0.97 (s, 3H), 0.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.8, 155.3, 140.7, 121.5, 79.2, 63.8, 57.0, 51.0, 50.1, 44.1, 39.8, 39.0, 38.1, 36.7, 32.0, 31.9, 31.7, 29.6, 28.6, 24.6, 23.0, 21.1, 19.5, 13.4.

FT-IR (film): 3371, 2937, 1702, 1514, 1365, 1236, 1172, 733 cm^{-1}.

MS (ESI) m/z $(M+Na)^+$ calcd for $C_{26}H_{41}NO_3Na$: 438.3, found: 438.4.

IV. Effect of Reaction Parameters



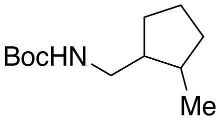
Workup of the irradiated mixture for GC analysis. A 20 mL vial was charged with a measured quantity of an internal standard (*n*-dodecane). The unpurified reaction mixture was then added to the 20 mL vial that contained the internal standard, ensuring quantitative transfer with EtOAc rinses (2 mL x 3). An aliquot was filtered through a pad of silica gel (eluting with EtOAc) into a GC vial, and the sample was subjected to GC analysis.

Table S1. Effect of reaction parameters. All data are the average of two runs.

Entry	Change from the "standard conditions"	Yield
1	none	91%
2	no **L1**	<1%
3	no CuBr	<1%
4	no hν	<1%
5	0.5 mol% **L1**	75%
6	5.0 mol% CuBr	81%
7	0.5 mol% **L1** and 5.0 mol% CuBr	65%
8	2.0 equiv carbamate, 2.0 equiv LiO*t*-Bu	52%
9	under air (capped vial)	21%
10	added H_2O (0.1 equiv)	85%
11	1.0 mol% $[Ru(bpy)_3](PF_6)_2$, instead of **L1**	<1%
12	1.0 mol% $[Ir(dtbbpy)(ppy)_2](PF_6)$, instead of **L1**	<1%
13	Hg, instead of blue-LED, lamp	94%
14	THF, instead of DME	90%
15	CuI, instead of CuBr	58%
16	CuCl, instead of CuBr	84%
17	$CuBr_2$, instead of CuBr	3%
18	Cu nanoparticle (60 - 80 nm), instead of CuBr	<1%
19	two, instead of three, blue-LED lamps	80%
20	one, instead of three, blue-LED lamps	55%
21	three 26 W CFLs, instead of three blue-LED lamps[c]	54%
22	NaO*t*-Bu, instead of LiO*t*-Bu	8%

23	KO*t*-Bu, instead of LiO*t*-Bu	3%
24	1.0 equiv H_2O	70%
25	1.0 mol% **1** and 9 mol% CuBr, instead of 1.0 mol% **L1** and 10 mol% CuBr	96%
26	1.0 mol%, instead of 10 mol%, CuBr	34%
27	1.0 mol% **1**, instead of 1.0 mol% **L1** and 10 mol% CuBr	33%
28	Toluene, instead of DME	44%
29	2-MeTHF, instead of DME	70%
30	MeCN, instead of DME	35%
31	no **L1**; Hg, instead of blue-LED, lamp	<1%

V. Mechanistic Studies



***tert*-Butyl ((2-methylcyclopentyl)methyl)carbamate. Eq 7.** The title compound was synthesized according to the General Procedure, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and 6-bromohept-1-ene (124 mg, 0.70 mmol) in DME (8 mL), and purified by column chromatography (7%→30% Et$_2$O/hexanes). Ratio of diastereomers: 4:1, which is consistent with that reported for the cyclization of the derived secondary alkyl radical.[6] Colorless oil. First run: 98 mg (66%). Second run: 94 mg (63%). Spectral data for the major diastereomer is provided below.

^{1}H NMR (400 MHz, CDCl$_3$) δ 4.52 (s, 1H), 3.18–3.03 (m, 1H), 3.06–2.90 (m, 1H), 2.05–1.99 (m, 1H), 1.93–1.88 (m, 1H), 1.73–1.61 (m, 2H), 1.56–1.45 (m, 2H), 1.39 (s, 9H), 1.32–1.20 (m, 2H), 0.80 (d, *J* = 7.1 Hz, 3H).

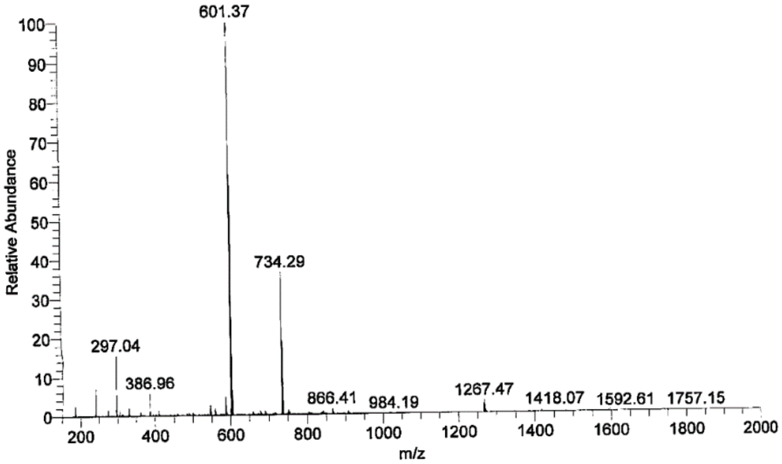
^{13}C NMR (101 MHz, CDCl$_3$) δ 156.1, 79.0, 43.2, 41.7, 35.3, 33.6, 30.4, 28.5, 22.6, 14.9.

FT-IR (film): 3350, 2955, 1694, 1520, 1366, 1250, 1174, 872 cm^{-1}.

MS (ESI) m/z (M)$^+$ calcd for C$_{12}$H$_{23}$NO$_2$: 213.2, found: 213.3.

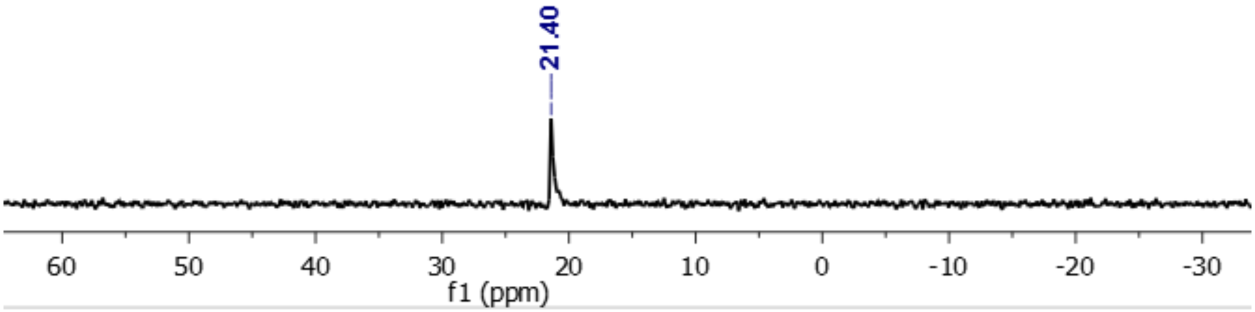
Monitoring the reaction mixture via mass spectrometry. Following General Procedure 2, a standard reaction mixture was prepared in an 8 mL vial, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL). The reaction mixture was subjected to irradiation with blue-LED lamps for 4 h. Next, the vial was then transferred to a nitrogen-filled glovebox, and an aliquot was passed through a PTFE syringe filter into a 4 mL vial. The filtrate was diluted and subjected to ESI analysis (Figure S6). A signal corresponding to copper complex **1** (m/z = 601.4) was detected.

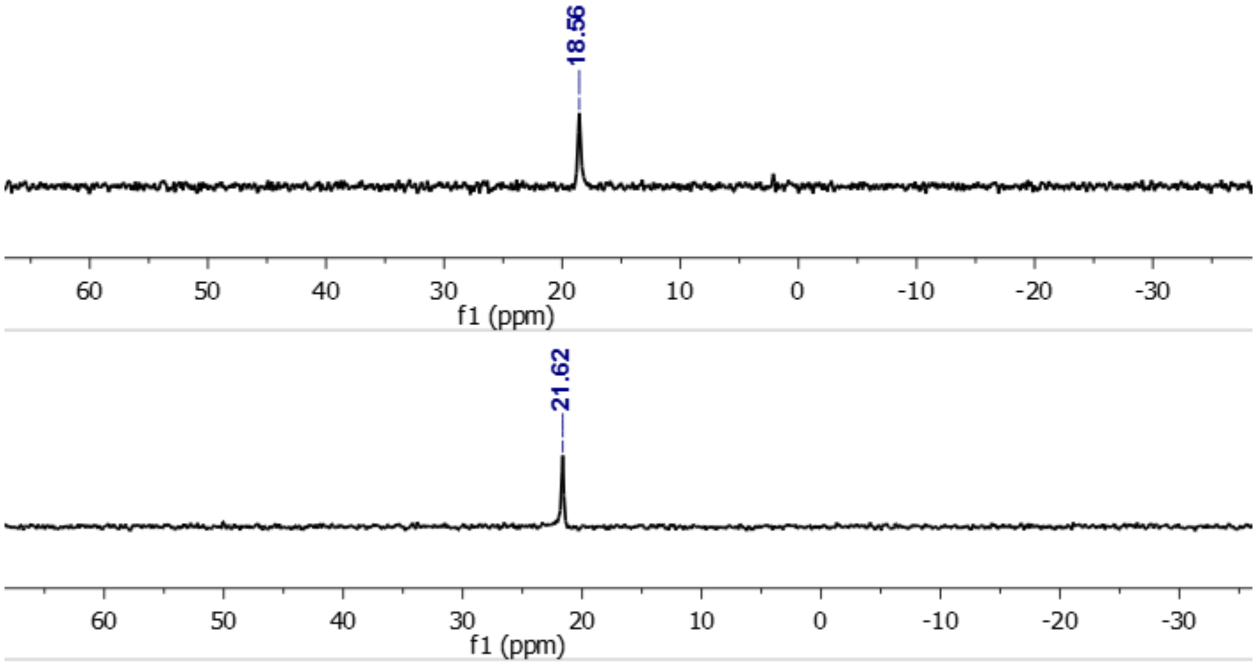
Figure S6. ESI-MS trace of a standard reaction mixture after 4 h of irradiation.



Monitoring the reaction mixture via ^{31}P NMR spectroscopy. Following General Procedure 2, a standard reaction mixture was prepared in an 8 mL vial, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL). An aliquot was transferred to an NMR tube under nitrogen, and a ^{31}P NMR spectrum was collected before irradiation (Figure S7, top). The remaining reaction mixture was subjected to irradiation with blue-LED lamps for 4 h. The vial was then transferred to a nitrogen-filled glovebox, and an aliquot was transferred to an NMR tube analysis (Figure S7, middle).

Figure S7. ^{31}P NMR spectra (162 MHz, rt): top: reaction mixture in DME prior to irradiation; middle: reaction mixture in DME after 4 h of irradiation; bottom: copper complex **1** in DME.





Light-on-light-off study. Following General Procedure 2, six standard reaction mixtures in 8 mL vials were prepared, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL). The six 8 mL vials were then subjected to irradiation with blue-LED lamps. After 2 h, the lamps were turned off, and one vial was removed from the irradiation setup for analysis. The remaining five vials were stirred in the absence of light in the water bath for an additional 2 h. Then, one vial was removed for analysis, and the lamps were turned back on to irradiate the remaining four reaction mixtures. After an additional 2 h of irradiation, the lamps were turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light in the water bath for an additional 2 h. Then, a vial was removed for analysis, and the lamps were turned back on to irradiate the remaining two reaction mixtures. After 2 h, the lamps were turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light in the water bath for an additional 2 h, and then it was analyzed.

Workup for ^{1}H NMR analysis. A 20 mL vial was charged with a measured quantity of an internal standard (1,3,5-trimethoxybenzene). The unpurified reaction mixture was then added to the 20 mL vial that contained the internal standard, ensuring quantitative transfer through EtOAc rinses (2 mL x 3). An aliquot was concentrated in vacuo, and CDCl$_3$ was added. Next, the solids were removed by filtration through a piece of cotton, and the filtrate was subjected to ^{1}H NMR analysis.

Figure S8. Effect of illumination on product formation. Blue lines denote periods during which the blue LED lamps were on, whereas yellow lines denote periods during which the lamps were off.

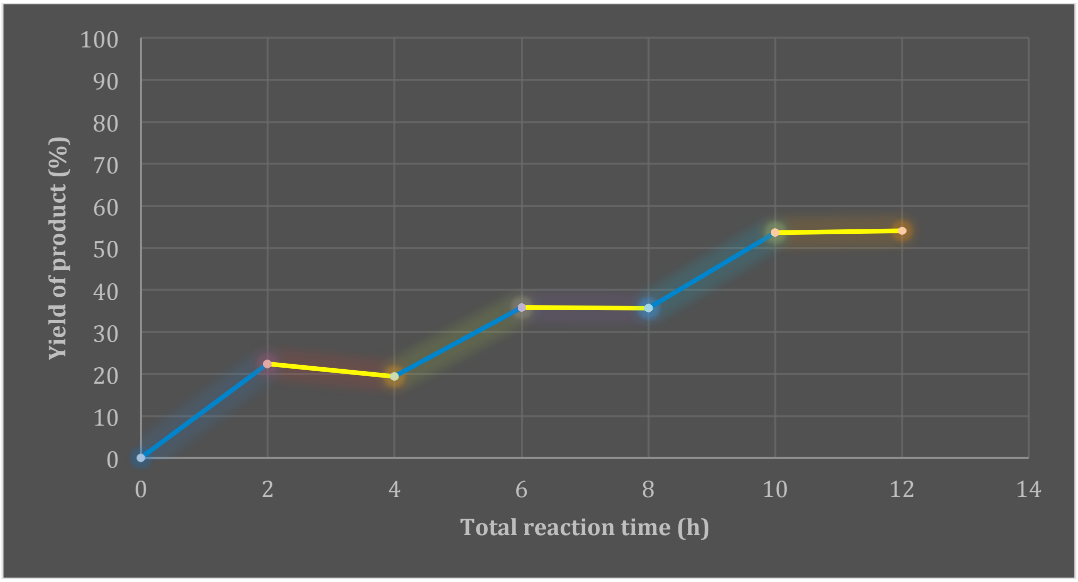


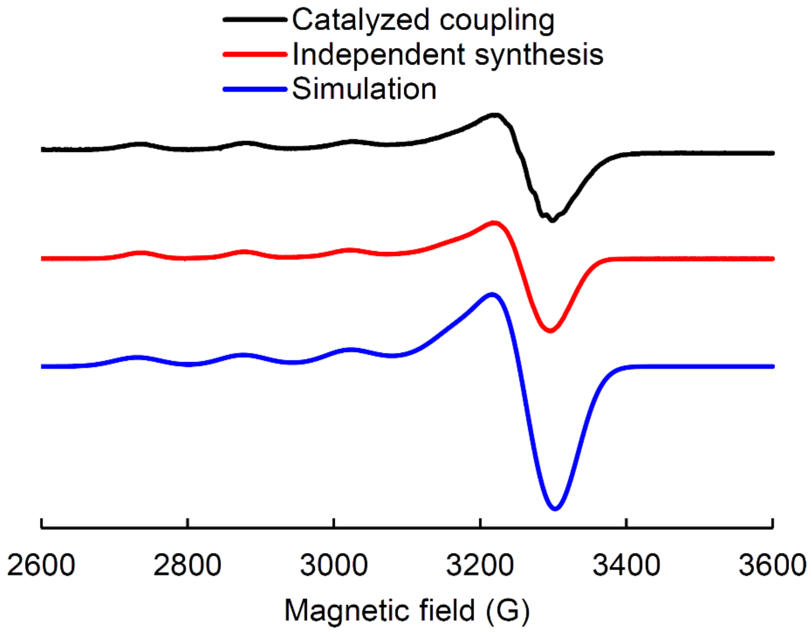
Table S2. Product formation as a function of time. All data are the average of two runs.

Total reaction period (h)	Total illumination period (h)	Yield
2	2	22%
4	2	19%
6	4	36%
8	4	36%
10	6	54%
12	6	54%

Detection of a Cu(II) intermediate during catalysis. Following General Procedure 2, a standard reaction mixture was prepared in an 8 mL vial, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), BocNH$_2$ (246 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL). The vial was then subjected to irradiation with blue-LED lamps. After 4 h, an aliquot (0.2 mL) was transferred via syringe to a 4 mL vial that contained a mixture of DME (0.6 mL) and 2-MeTHF (0.2 mL) under nitrogen. The diluted reaction mixture was then transferred via syringe under nitrogen to an EPR tube for X-band EPR measurement at 77 K.

Generation of a Cu(II) complex via independent synthesis. A 4 mL vial was charged with $CuBr_2$ (2.2 mg, 0.0099 mmol), $BocNH_2$ (11.7 mg, 0.10 mmol, 10 equiv), LiO*t*-Bu (8.0 mg, 0.10 mmol, 10 equiv), and a magnetic stir bar. DME (1 mL) was added to the vial, and the mixture was stirred at room temperature for 10 min. An aliquot (0.15 mL) was then transferred to another 4 mL vial that contained 2-MeTHF (0.05 mL), and the mixture was transferred to an EPR tube for X-band EPR measurement at 77 K. Simulated values are as follows: g = [2.276, 2.063, 2.058], A_{Cu} = [0, 0, 439] MHz, lw = 6.2 MHz.

Figure S9. X-band EPR spectra (9.4 GHz, 77 K): black: catalyzed coupling of $BocNH_2$ with 2-bromo-4-phenylbutane; red: mixture of $CuBr_2$, $BocNH_2$ (10 equiv), and LiO*t*-Bu (10 equiv); blue: simulation of red spectrum. g = [2.276, 2.063, 2.058], A_{Cu} = [0, 0, 439] MHz, lw = 6.2 MHz.

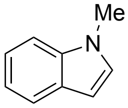
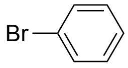
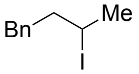
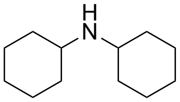
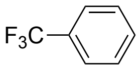
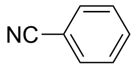
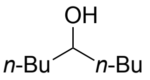
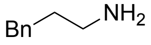
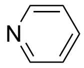
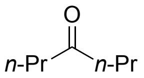
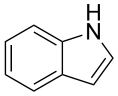
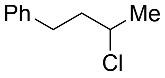
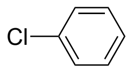
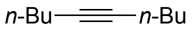
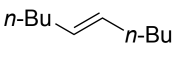
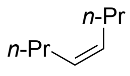


VI. Effect of Additives

Following General Procedure 2, a standard reaction mixture was prepared in an 8 mL vial, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), $BocNH_2$ (246 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL). Next, the additive (0.7 mmol) was added, and the vial was capped and subjected to irradiation with blue-LED lamps.

A 20 mL vial was charged with a measured quantity of an internal standard (1,3,5-trimethoxybenzene). The unpurified reaction mixture was then added to the 20 mL vial that contained the internal standard, ensuring quantitative transfer through EtOAc rinses (2 mL x 3). An aliquot was filtered through a pad of silica gel (eluting with EtOAc) into a GC vial, and the sample was subjected to GC analysis. Another aliquot was concentrated in vacuo, and $CDCl_3$ was added; next, the solids were removed by filtration through a piece of cotton, and the filtrate was subjected to ^{1}H NMR analysis.

Table S3. Effect of additives.

Compatible: >70% yield of coupling product >80% recovery of additive	**Largely compatible:** 40–70% yield of coupling product >70% recovery of additive	**Problematic:** $\leq$30% yield of coupling product
		
		
		
		
		
		
		
		
		
n-Pr−CN		

VII. DFT Calculations

Geometry optimizations, single-point calculations, frequency calculations, and time-dependent calculations were performed using the Gaussian 09 (Rev B.01) suite of programs with the B3LYP functional and the 6-31G* basis set for all atoms.[7] Frequency calculations were performed on optimized geometries to ensure true minima.

Figure S10. DFT-generated frontier molecular orbitals (MO = 160, MO = 161, MO = 162, MO = 163, MO = 164, MO = 165) of copper complex **1**.

MO	Occupancy	Relative Energy
165	☐	0.02629
164	☐	0.00026
163	☐	-0.01062
162	⥮	-0.15466
161	⥮	-0.17822
160	⥮	-0.17963

Figure S11. HOMO (MO = 162), HOMO–1 (MO = 161), and HOMO-2 (MO = 162) of copper complex **1** (H atoms are omitted for clarity).

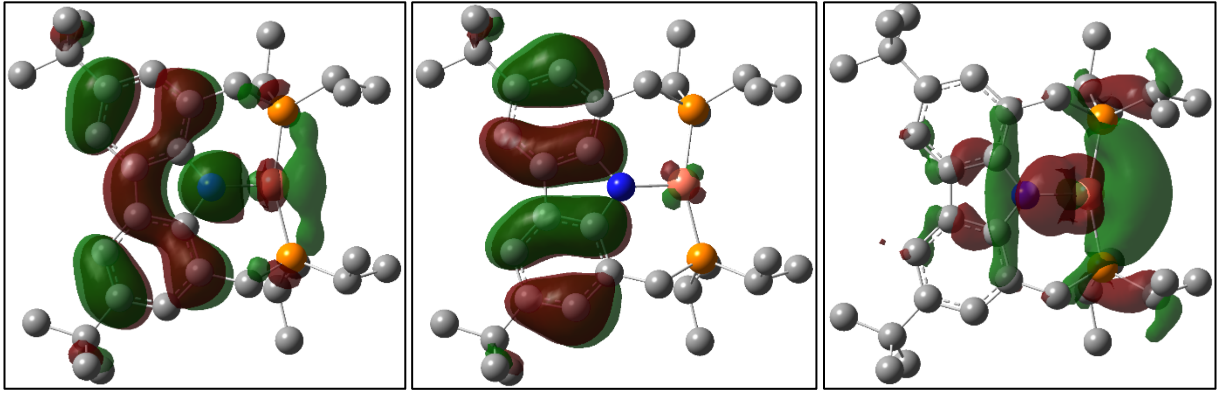


Figure S12. LUMO (MO = 163), LUMO+1 (MO = 164), and LUMO+2 (MO = 165) of copper complex **1** (H atoms are omitted for clarity).

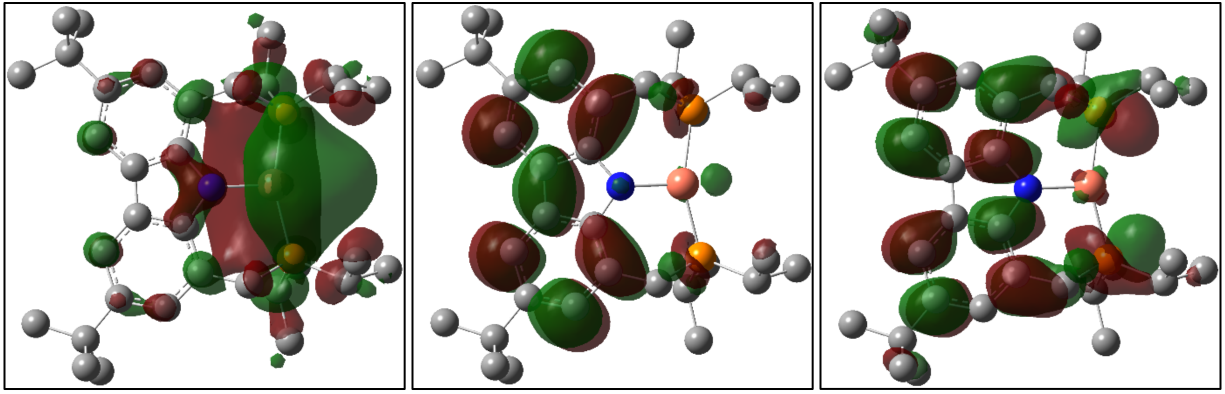


Figure S13. TD-DFT results: Orbital compositions of the calculated singlet excitations (first three) of copper complex **1**. Transitions of significance are in bold.

Excited State 1: 393 nm (*f* =0.0240)	160 (HOMO-2)	⟶	163 (LUMO)	(0.19)
	162 (HOMO)	⟶	**163 (LUMO)**	(0.67)
Excited State 2: 360 nm (*f* =0.0056)	**160 (HOMO-2)**	⟶	**163 (LUMO)**	(0.66)
	162 (HOMO)	⟶	163 (LUMO)	(-0.19)
Excited State 3: 344 nm (*f* =0.0772)	161 (HOMO-1)	⟶	165 (LUMO+2)	(-0.11)
	162 (HOMO)	⟶	**164 (LUMO+1)**	(0.69)

Figure S14. Calculated absorption spectrum of copper complex **1**.

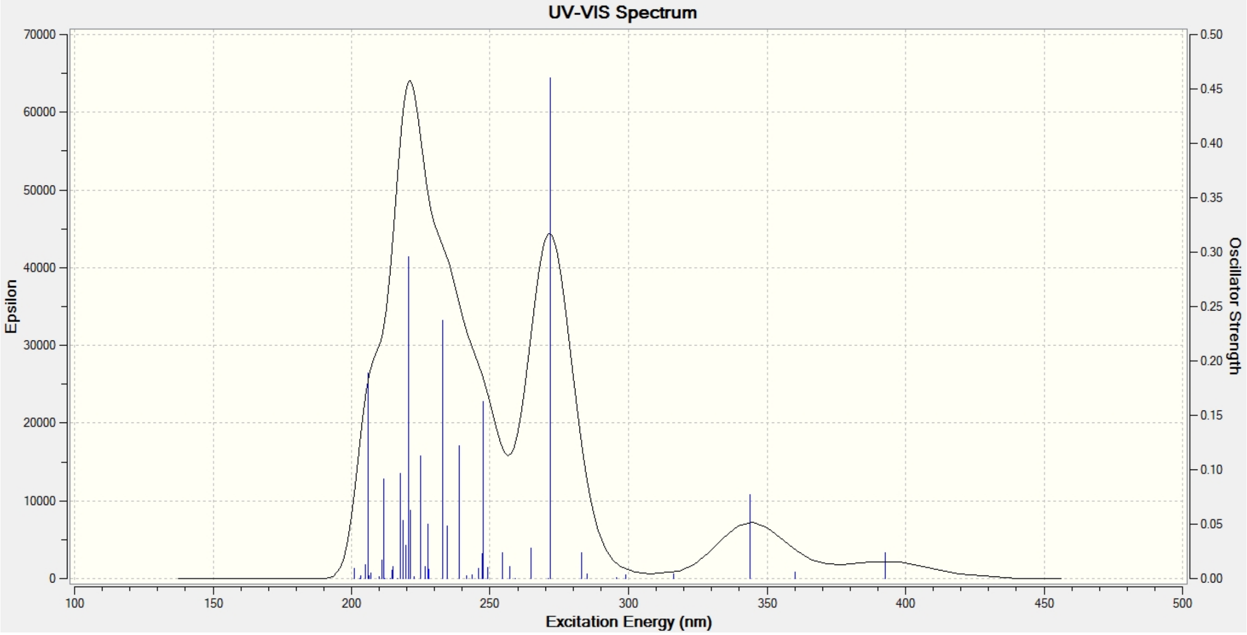


Figure S15. Observed absorption spectrum of copper complex **1** in THF.

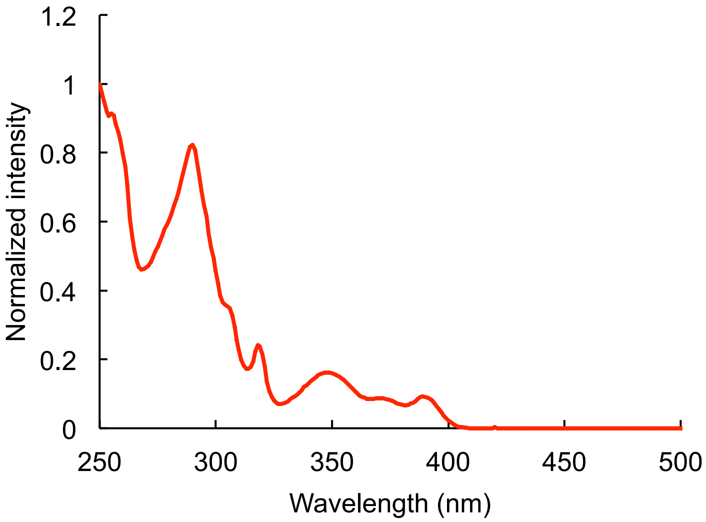


Figure S16. DFT-generated spin-density plot of the one-electron oxidized form of copper complex **1** (14.8% on Cu, 34.5% on N).

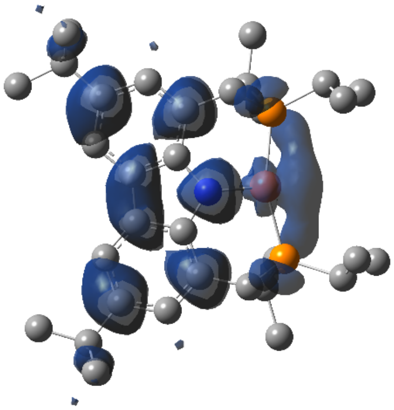


Figure S17. DFT-generated frontier molecular orbitals (MO = 160, MO = 161, MO = 162, MO = 163, MO = 164, MO = 165) of the one-electron oxidized form of copper complex **1**.

Alpha MOs

MO	Occupancy	Relative Energy
165	☐	-0.10391
164	☐	-0.11816
163	☐	-0.13006
162	↑	-0.29767
161	↑	-0.31103
160	↑	-0.31235

Beta MOs

MO	Occupancy	Relative Energy
165	☐	-0.09689
164	☐	-0.11672
163	☐	-0.12478
162	☐	-0.23791
161	↓	-0.29973
160	↓	-0.31070

Figure S18. Alpha MOs: HOMO (MO = 162), HOMO–1 (MO = 161), and HOMO-2 (MO = 160) of the one-electron oxidized form of copper complex **1** (H atoms are omitted for clarity).

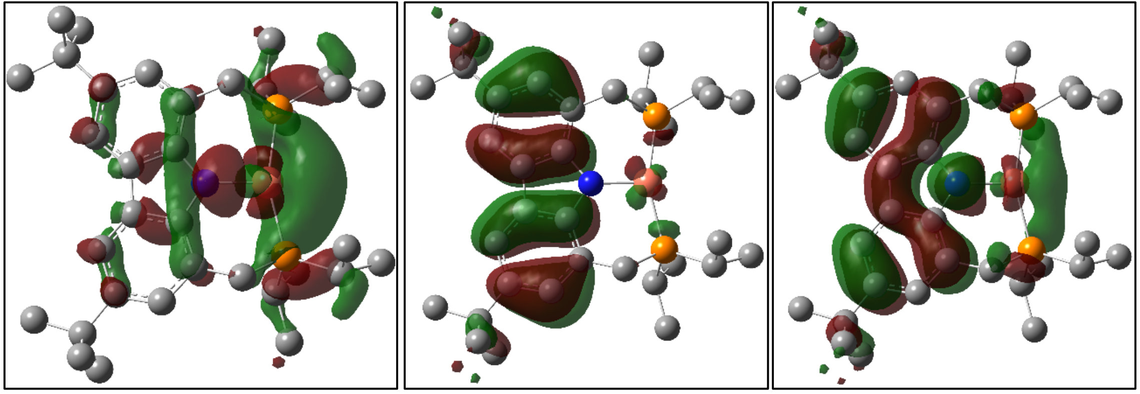


Figure S19. Alpha MOs: LUMO (MO = 163), LUMO+1 (MO = 164), and LUMO+2 (MO = 165) of copper complex **1** (H atoms are omitted for clarity).

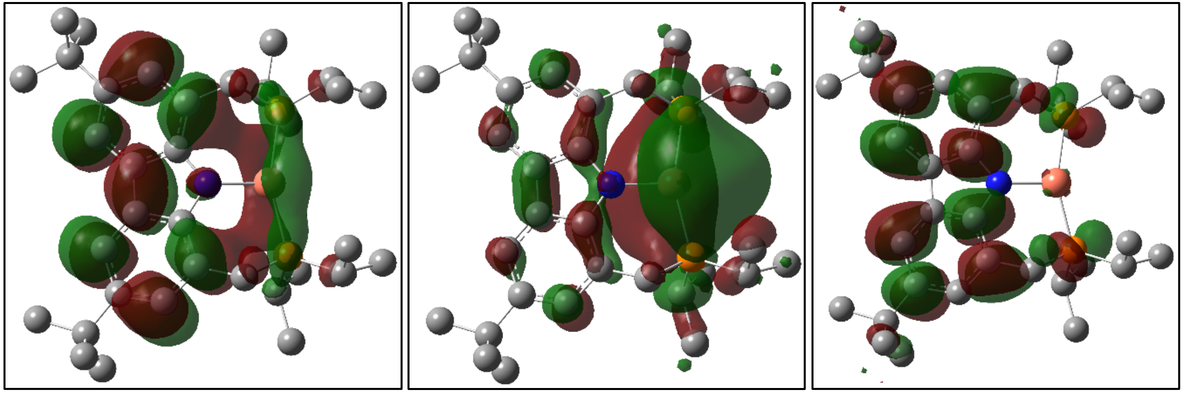


Figure S20. Beta MOs: LUMO (MO = 162), HOMO (MO = 161), and HOMO-1 (MO = 160) of the one-electron oxidized form of copper complex **1** (H atoms are omitted for clarity).

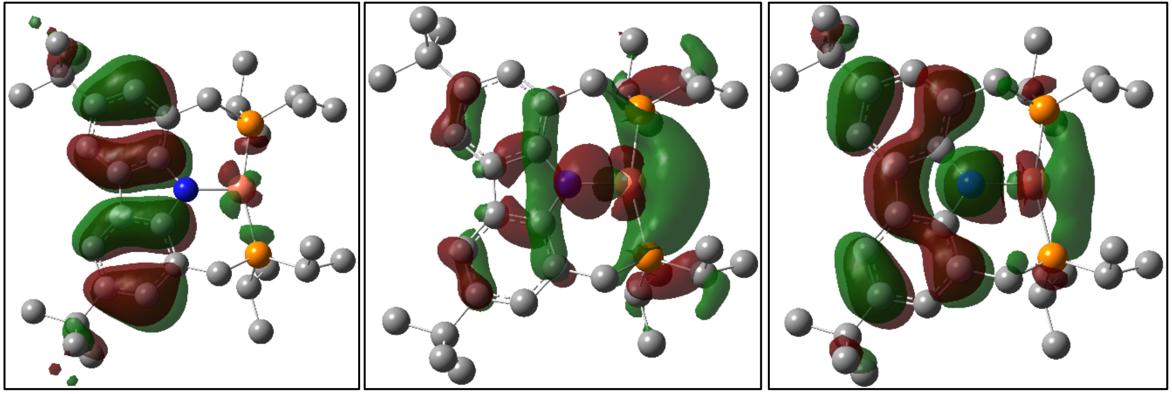
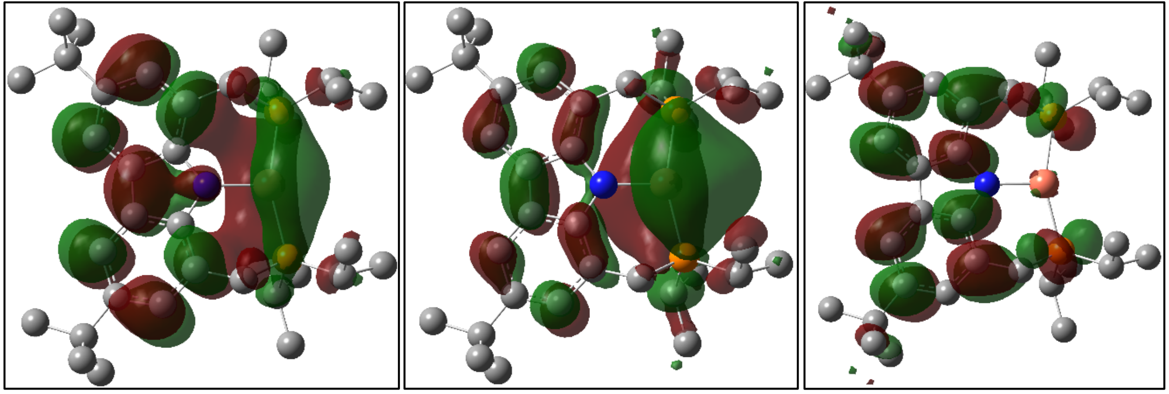
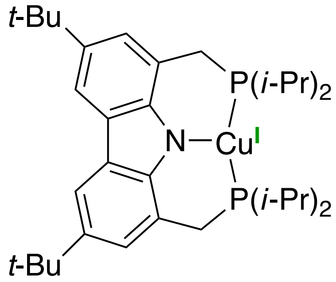


Figure S21. Beta MOs: LUMO+1 (MO = 163), LUMO+2 (MO = 164), and LUMO+3 (MO = 165) of the one-electron oxidized form of copper complex **1** (H atoms are omitted for clarity).



VIII. X-Ray Crystallographic Data



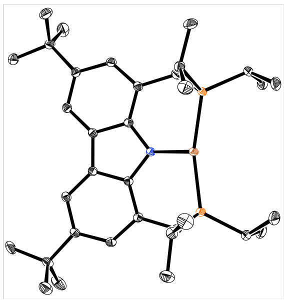


Table S4. Crystal data and structure refinement for copper complex **1**.

Identification code	**Complex 1**
Empirical formula	$C_{34}H_{54}NP_2Cu$
Formula weight	602.26
Temperature/K	100.05
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.4490(9)
b/Å	22.9148(14)
c/Å	23.1633(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6607.7(7)
Z	8
ρ_{calc}g/cm^3	1.211
μ/mm^{-1}	0.780
F(000)	2592.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.516 to 66.098
Index ranges	$-18 \le h \le 18$, $-34 \le k \le 32$, $-28 \le l \le 35$
Reflections collected	103697
Independent reflections	11695 [R_{int} = 0.0580, R_{sigma} = 0.0339]
Data/restraints/parameters	11695/0/357
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.1284
Final R indexes [all data]	R_1 = 0.0550, wR_2 = 0.1405
Largest diff. peak/hole / e Å^{-3}	0.76/-0.69

Table S5. Fractional atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters (Å$^2\times10^3$) for complex **1**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cu1	8134.6(2)	3559.3(2)	294.2(2)	12.50(6)
P2	9428.5(3)	2905.6(2)	196.9(2)	12.76(8)
P3	7233.1(3)	4381.6(2)	205.0(2)	12.32(8)
N1	7194.9(10)	3150.1(5)	848.7(5)	12.0(2)
C24	8167.6(11)	1844.6(6)	2003.2(6)	13.5(2)
C26	6469.4(11)	3440.0(5)	1200.3(6)	12.2(2)
C31	8745.3(12)	2222.8(5)	412.9(6)	14.4(2)
C27	6373.7(11)	3171.5(5)	1751.1(6)	12.1(2)
C28	5640.2(11)	3383.1(6)	2160.4(6)	13.9(2)
C32	8554.5(13)	1372.6(6)	2423.7(7)	17.2(3)
C25	7408.6(11)	2263.1(6)	2148.7(6)	14.0(2)
C23	8594.2(11)	1850.1(5)	1436.6(6)	13.6(2)
C11	10482.9(12)	2957.7(6)	755.7(6)	16.9(3)
C22	8308.5(11)	2256.0(5)	1019.2(6)	12.5(2)
C29	5004.9(11)	3863.9(6)	2031.1(6)	14.0(2)
C30	5871.9(11)	4205.1(6)	467.6(6)	15.5(3)
C21	7570.0(11)	2691.8(5)	1183.7(6)	11.8(2)
C20	11192.1(14)	2416.0(7)	810.9(7)	24.6(3)
C37	4144.0(13)	3773.9(6)	3023.3(7)	20.2(3)
C33	8014.0(15)	1427.5(8)	3013.6(8)	28.0(4)
C39	4340.0(15)	4747.5(7)	2573.0(8)	27.3(4)
C4	5839.5(11)	3932.0(5)	1061.9(6)	13.1(2)
C41	8868.4(14)	5047.2(7)	731.1(7)	24.2(3)
C38	3031.9(13)	4020.1(9)	2166.4(8)	27.9(4)
C42	7096.8(14)	5565.1(6)	568.9(8)	22.6(3)
C8	7105.8(11)	2686.3(5)	1741.8(6)	12.4(2)
C45	8062.8(13)	4880.5(7)	-786.5(7)	21.4(3)
C34	8286.5(16)	764.8(7)	2175.6(8)	29.7(4)
C40	7644.0(12)	4981.0(6)	696.4(6)	15.9(3)
C36	4142.2(12)	4096.6(6)	2444.6(6)	17.0(3)
C13	5134.5(11)	4132.7(6)	1483.1(6)	14.7(2)
C35	9771.1(14)	1422.5(7)	2509.7(8)	24.8(3)
C47	9257.9(14)	2432.7(8)	-898.3(7)	25.5(3)
C48	10490.3(15)	3291.1(7)	-785.3(7)	25.7(3)
C46	10065.3(13)	2732.3(6)	-500.8(6)	17.8(3)
C43	6987.5(12)	4709.0(6)	-511.9(6)	15.9(3)
C44	6380.7(14)	4278.4(7)	-901.0(6)	22.4(3)
C1	11159.6(15)	3512.0(7)	698.6(8)	26.9(3)

Table S6. Anisotropic displacement parameters ($Å^2 \times 10^3$) for Complex 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	14.75(10)	8.87(9)	13.88(10)	1.67(5)	2.58(6)	1.81(5)
P2	15.32(17)	9.46(15)	13.52(17)	0.79(11)	2.63(12)	1.57(11)
P3	15.15(18)	9.33(14)	12.48(16)	2.07(11)	2.14(12)	1.58(12)
N1	14.5(5)	8.5(4)	13.0(5)	0.9(4)	1.2(4)	0.4(4)
C24	15.7(6)	9.4(5)	15.4(6)	2.4(4)	-0.9(5)	-0.7(4)
C26	13.7(6)	10.1(5)	12.9(6)	-0.2(4)	0.2(5)	-0.5(4)
C31	19.4(7)	8.6(5)	15.1(6)	-0.9(4)	2.2(5)	0.5(4)
C27	13.3(6)	9.8(5)	13.2(6)	1.0(4)	-0.1(5)	-1.1(4)
C28	15.6(6)	12.7(5)	13.3(6)	0.9(5)	1.8(5)	-0.9(4)
C32	18.9(7)	14.0(5)	18.6(7)	5.0(5)	-0.7(5)	1.0(5)
C25	15.9(6)	12.3(5)	13.9(6)	2.0(4)	-0.1(5)	-1.3(4)
C23	15.8(6)	8.5(5)	16.6(6)	-0.4(4)	0.1(5)	-0.4(4)
C11	17.0(7)	15.9(6)	17.8(7)	0.1(5)	0.0(5)	-1.2(5)
C22	15.4(6)	8.4(5)	13.7(6)	-0.8(4)	0.8(5)	-1.6(4)
C29	15.1(6)	12.5(5)	14.4(6)	0.1(4)	2.8(5)	-0.6(4)
C30	16.3(6)	14.5(6)	15.7(6)	4.0(5)	0.5(5)	1.3(5)
C21	13.8(6)	8.5(5)	13.1(6)	0.5(4)	-0.1(4)	-1.2(4)
C20	19.3(7)	24.4(7)	30.1(9)	4.4(6)	-2.3(6)	4.0(6)
C37	22.7(7)	20.2(6)	17.7(7)	1.9(5)	5.9(6)	1.8(5)
C33	30.2(9)	34.8(9)	19.0(8)	14.7(6)	3.5(6)	8.0(7)
C39	40.6(10)	15.6(6)	25.7(8)	-0.7(6)	14.3(7)	4.6(6)
C4	13.8(6)	11.0(5)	14.5(6)	1.8(4)	1.3(5)	-0.5(4)
C41	24.0(8)	20.8(7)	28.0(8)	0.0(6)	-2.7(6)	-1.6(6)
C38	17.3(8)	41.2(10)	25.2(8)	5.4(7)	4.2(6)	3.5(6)
C42	27.4(8)	13.9(6)	26.4(8)	-3.6(5)	3.6(6)	3.9(5)
C8	13.7(6)	10.3(5)	13.2(6)	0.6(4)	0.4(5)	-0.7(4)
C45	29.9(8)	17.5(6)	16.8(7)	4.0(5)	5.7(6)	-2.1(5)
C34	41.6(10)	12.8(6)	34.9(10)	8.0(6)	-10.4(8)	-3.2(6)
C40	19.3(7)	13.5(5)	15.1(6)	-0.7(5)	2.4(5)	-1.0(5)
C36	17.3(6)	16.1(6)	17.7(7)	2.0(5)	5.6(5)	2.8(5)
C13	14.9(6)	12.6(5)	16.5(6)	1.6(5)	2.3(5)	1.4(4)
C35	20.0(8)	28.4(8)	26.0(8)	5.9(6)	-4.2(6)	2.6(6)
C47	27.3(8)	33.2(8)	16.1(7)	-3.9(6)	3.3(6)	2.3(6)
C48	31.0(9)	23.9(7)	22.1(8)	5.7(6)	10.6(6)	1.7(6)
C46	21.7(7)	16.5(6)	15.2(7)	2.1(5)	5.2(5)	5.2(5)
C43	21.7(7)	12.6(5)	13.3(6)	2.6(5)	1.8(5)	3.4(5)
C44	27.7(8)	24.3(7)	15.3(7)	-0.9(6)	-0.1(6)	-1.0(6)
C1	25.1(8)	21.7(7)	33.8(9)	0.8(6)	-2.5(7)	-7.7(6)

Table S7. Bond lengths for complex **1.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	P2	2.2112(4)	C32	C34	1.543(2)
Cu1	P3	2.2029(4)	C32	C35	1.532(2)
Cu1	N1	1.9741(11)	C25	C8	1.4039(18)
P2	C31	1.8497(14)	C23	C22	1.3878(18)
P2	C11	1.8474(15)	C11	C20	1.529(2)
P2	C46	1.8434(15)	C11	C1	1.530(2)
P3	C30	1.8452(15)	C22	C21	1.4097(18)
P3	C40	1.8557(14)	C29	C36	1.5347(19)
P3	C43	1.8477(15)	C29	C13	1.4201(19)
N1	C26	1.3857(17)	C30	C4	1.5127(19)
N1	C21	1.3868(16)	C21	C8	1.4162(19)
C24	C32	1.5332(19)	C37	C36	1.531(2)
C24	C25	1.3878(19)	C39	C36	1.541(2)
C24	C23	1.4160(19)	C4	C13	1.3906(19)
C26	C27	1.4214(18)	C41	C40	1.534(2)
C26	C4	1.4103(18)	C38	C36	1.535(2)
C31	C22	1.5080(19)	C42	C40	1.530(2)
C27	C28	1.4028(19)	C45	C43	1.533(2)
C27	C8	1.4379(18)	C47	C46	1.526(2)
C28	C29	1.3889(19)	C48	C46	1.534(2)
C32	C33	1.528(2)	C43	C44	1.535(2)

Table S8. Bond angles for complex **1.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P3	Cu1	P2	160.224(16)	C22	C23	C24	123.75(12)
N1	Cu1	P2	100.15(3)	C20	C11	P2	114.61(11)
N1	Cu1	P3	99.52(3)	C20	C11	C1	111.31(13)
C31	P2	Cu1	102.15(5)	C1	C11	P2	112.60(11)
C11	P2	Cu1	113.73(5)	C23	C22	C31	121.50(12)
C11	P2	C31	101.06(7)	C23	C22	C21	116.98(13)
C46	P2	Cu1	123.27(5)	C21	C22	C31	121.50(12)
C46	P2	C31	104.64(6)	C28	C29	C36	122.65(12)
C46	P2	C11	108.82(7)	C28	C29	C13	118.17(12)
C30	P3	Cu1	104.45(4)	C13	C29	C36	119.12(12)
C30	P3	C40	102.31(7)	C4	C30	P3	114.53(10)
C30	P3	C43	103.49(7)	N1	C21	C22	127.22(12)
C40	P3	Cu1	115.80(5)	N1	C21	C8	112.35(11)
C43	P3	Cu1	121.06(5)	C22	C21	C8	120.43(12)
C43	P3	C40	107.23(7)	C26	C4	C30	121.52(12)
C26	N1	Cu1	122.75(8)	C13	C4	C26	117.12(12)
C26	N1	C21	104.69(11)	C13	C4	C30	121.23(12)
C21	N1	Cu1	121.61(9)	C25	C8	C27	133.97(13)
C25	C24	C32	123.17(13)	C25	C8	C21	120.63(12)
C25	C24	C23	118.31(12)	C21	C8	C27	105.39(11)
C23	C24	C32	118.52(12)	C41	C40	P3	112.29(10)
N1	C26	C27	112.01(11)	C42	C40	P3	113.97(11)
N1	C26	C4	127.73(12)	C42	C40	C41	111.47(12)
C4	C26	C27	120.23(12)	C29	C36	C39	110.18(12)
C22	C31	P2	112.03(9)	C29	C36	C38	109.18(13)
C26	C27	C8	105.55(11)	C37	C36	C29	112.19(12)
C28	C27	C26	120.77(12)	C37	C36	C39	107.36(13)
C28	C27	C8	133.63(12)	C37	C36	C38	108.27(13)
C29	C28	C27	119.94(12)	C38	C36	C39	109.61(14)
C24	C32	C34	109.40(12)	C4	C13	C29	123.73(12)
C33	C32	C24	111.81(12)	C47	C46	P2	110.03(11)
C33	C32	C34	108.19(14)	C47	C46	C48	110.09(13)
C33	C32	C35	108.24(14)	C48	C46	P2	110.19(10)
C35	C32	C24	109.91(12)	C45	C43	P3	109.42(10)
C35	C32	C34	109.25(13)	C45	C43	C44	110.54(12)
C24	C25	C8	119.80(13)	C44	C43	P3	110.37(10)

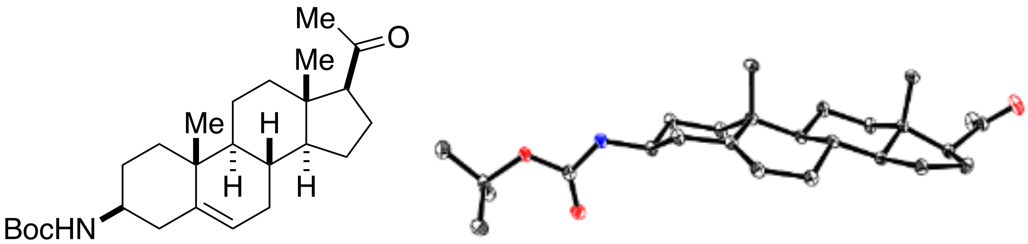


Table S9. Crystal data and structure refinement for Product (Eq 6).

Identification code	Product (Eq 6)
Empirical formula	$C_{26}H_{41}NO_3$
Formula weight	415.60
Temperature/K	100.02
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.1123(3)
b/Å	19.6726(8)
c/Å	20.4876(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2463.53(18)
Z	4
ρ_{calc}g/cm^3	1.121
μ/mm^{-1}	0.072
F(000)	912.0
Crystal size/mm^3	0.6 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.484 to 68.706
Index ranges	$-9 \leq h \leq 9$, $-30 \leq k \leq 30$, $-31 \leq l \leq 30$
Reflections collected	52546
Independent reflections	9627 [R_{int} = 0.0600, R_{sigma} = 0.0711]
Data/restraints/parameters	9627/0/284
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1152
Final R indexes [all data]	R_1 = 0.0860, wR_2 = 0.1256
Largest diff. peak/hole / e Å^{-3}	0.37/-0.28
Flack parameter	-0.1(3)

Table S10. Anisotropic Displacement Parameters (Å^2×10^3) for Product (Eq 6). The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a^{*2}U$_{11}$+2hka*b*U$_{12}$+…].

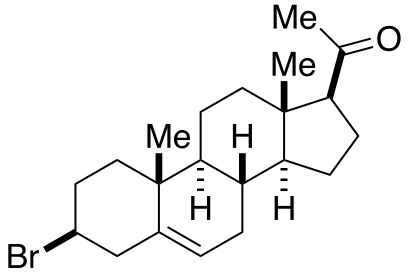
Atom	*x*	*y*	*z*	U(eq)
O(001)	857(2)	8171.2(6)	2159.5(6)	13.8(3)
O(002)	81(2)	8170.0(7)	3250.1(6)	17.5(3)
O(003)	10051(3)	3536.6(7)	6814.1(8)	23.7(3)
N(004)	2602(3)	7454.0(7)	2801.6(7)	14.0(3)
C(005)	1081(3)	7950.1(8)	2784.8(9)	11.7(3)
C(006)	8283(3)	3795.3(9)	6710.5(9)	14.1(3)
C(007)	7807(3)	5795.8(8)	5145.8(8)	9.8(3)
C(008)	7603(3)	4694.7(8)	5816.5(8)	9.6(3)
C(009)	9286(3)	4305.1(9)	5403.7(9)	12.7(3)
C(00A)	7410(3)	6931.2(9)	4587.8(9)	13.7(3)
C(00B)	6174(3)	6661.2(8)	4121.6(9)	10.7(3)
C(00C)	5538(3)	5642.9(8)	4851.6(8)	9.2(3)
C(00D)	5290(3)	4567.4(9)	5568.5(9)	12.1(3)
C(00E)	5265(3)	5939.7(8)	4151.2(8)	9.3(3)
C(00F)	7972(3)	5468.2(8)	5817.5(8)	10.5(3)
C(00G)	4973(3)	4878.6(8)	4887.9(9)	12.2(3)
C(00H)	8022(3)	4544.5(8)	6553.2(8)	11.4(3)
C(00I)	2791(3)	5971.6(9)	3991.7(9)	13.2(3)
C(00J)	2235(3)	6351.2(9)	3361.7(9)	13.9(3)
C(00K)	8114(3)	6565.6(9)	5195.6(9)	13.6(3)
C(00L)	10086(3)	5567.9(9)	6209.2(9)	14.8(3)
C(00M)	3106(3)	7076.6(9)	3397.5(9)	12.9(3)
C(00N)	5580(3)	7073.8(9)	3521.8(9)	13.3(3)
C(00O)	-721(3)	8712.0(9)	2001.6(9)	14.1(3)
C(00P)	6442(3)	5499.4(9)	3637.3(9)	13.0(3)
C(00Q)	10026(3)	4987.5(9)	6725.0(9)	14.6(3)
C(00R)	-3049(3)	8472.5(10)	2128.6(10)	18.8(4)
C(00S)	-171(4)	9357.1(9)	2374.3(10)	19.6(4)
C(00T)	6218(4)	3379.3(10)	6735.3(11)	22.7(4)
C(00U)	-323(4)	8817.4(10)	1277.9(10)	23.2(4)

Table S11. Bond lengths for Product (Eq 6).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(001)	C(005)	1.360(2)	C(00B)	C(00E)	1.525(2)
O(001)	C(00O)	1.472(2)	C(00B)	C(00N)	1.517(2)
O(002)	C(005)	1.212(2)	C(00C)	C(00E)	1.558(2)
O(003)	C(006)	1.213(2)	C(00C)	C(00G)	1.544(2)
N(004)	C(005)	1.348(2)	C(00D)	C(00G)	1.535(2)
N(004)	C(00M)	1.462(2)	C(00E)	C(00I)	1.548(3)
C(006)	C(00H)	1.517(2)	C(00E)	C(00P)	1.541(2)
C(006)	C(00T)	1.505(3)	C(00F)	C(00L)	1.533(3)
C(007)	C(00C)	1.542(2)	C(00H)	C(00Q)	1.544(3)
C(007)	C(00F)	1.523(2)	C(00I)	C(00J)	1.529(2)
C(007)	C(00K)	1.529(2)	C(00J)	C(00M)	1.525(2)
C(008)	C(009)	1.537(2)	C(00L)	C(00Q)	1.556(2)
C(008)	C(00D)	1.523(3)	C(00M)	C(00N)	1.533(3)
C(008)	C(00F)	1.538(2)	C(00O)	C(00R)	1.521(3)
C(008)	C(00H)	1.559(2)	C(00O)	C(00S)	1.519(3)
C(00A)	C(00B)	1.329(3)	C(00O)	C(00U)	1.517(3)
C(00A)	C(00K)	1.501(2)			

Table S12. Bond Angles for Product (Eq 6).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(005)	O(001)	C(00O)	120.29(14)	C(00B)	C(00E)	C(00P)	109.02(14)
C(005)	N(004)	C(00M)	122.28(15)	C(00I)	C(00E)	C(00C)	108.31(14)
O(002)	C(005)	O(001)	125.15(16)	C(00P)	C(00E)	C(00C)	111.62(13)
O(002)	C(005)	N(004)	125.87(16)	C(00P)	C(00E)	C(00I)	109.54(15)
N(004)	C(005)	O(001)	108.97(15)	C(007)	C(00F)	C(008)	114.06(13)
O(003)	C(006)	C(00H)	122.56(17)	C(007)	C(00F)	C(00L)	118.33(15)
O(003)	C(006)	C(00T)	120.88(17)	C(00L)	C(00F)	C(008)	104.52(14)
C(00T)	C(006)	C(00H)	116.56(17)	C(00D)	C(00G)	C(00C)	113.82(14)
C(00F)	C(007)	C(00C)	109.29(14)	C(006)	C(00H)	C(008)	114.01(14)
C(00F)	C(007)	C(00K)	110.53(14)	C(006)	C(00H)	C(00Q)	114.62(15)
C(00K)	C(007)	C(00C)	109.24(14)	C(00Q)	C(00H)	C(008)	104.11(13)
C(009)	C(008)	C(00F)	113.34(14)	C(00J)	C(00I)	C(00E)	114.53(15)
C(009)	C(008)	C(00H)	109.17(14)	C(00M)	C(00J)	C(00I)	109.79(15)
C(00D)	C(008)	C(009)	110.85(14)	C(00A)	C(00K)	C(007)	112.59(14)
C(00D)	C(008)	C(00F)	107.41(14)	C(00F)	C(00L)	C(00Q)	103.99(15)
C(00D)	C(008)	C(00H)	116.36(14)	N(004)	C(00M)	C(00J)	111.19(15)
C(00F)	C(008)	C(00H)	99.33(13)	N(004)	C(00M)	C(00N)	110.37(15)
C(00B)	C(00A)	C(00K)	124.59(16)	C(00J)	C(00M)	C(00N)	110.42(15)
C(00A)	C(00B)	C(00E)	123.41(15)	C(00B)	C(00N)	C(00M)	111.87(15)
C(00A)	C(00B)	C(00N)	120.30(15)	O(001)	C(00O)	C(00R)	110.57(14)
C(00N)	C(00B)	C(00E)	116.29(15)	O(001)	C(00O)	C(00S)	110.38(16)
C(007)	C(00C)	C(00E)	112.54(14)	O(001)	C(00O)	C(00U)	102.03(15)
C(007)	C(00C)	C(00G)	111.84(14)	C(00S)	C(00O)	C(00R)	112.34(17)
C(00G)	C(00C)	C(00E)	112.66(13)	C(00U)	C(00O)	C(00R)	111.07(17)
C(008)	C(00D)	C(00G)	110.75(14)	C(00U)	C(00O)	C(00S)	109.98(16)
C(00B)	C(00E)	C(00C)	110.25(14)	C(00H)	C(00Q)	C(00L)	106.14(15)
C(00B)	C(00E)	C(00I)	108.03(14)				



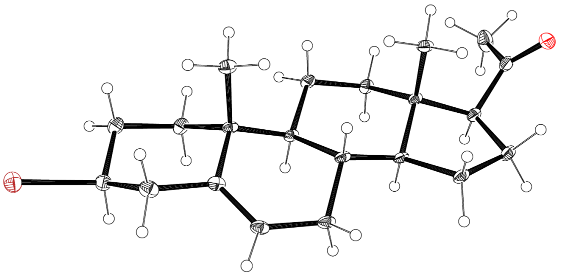


Table S13. Crystal data and structure refinement for Substrate (Eq 6).

Identification code	Substrate (Eq 6)
Empirical formula	$C_{21}H_{31}BrO$
Formula weight	379.37
Temperature/K	99.98
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.8610(3)
b/Å	9.0451(4)
c/Å	25.8041(14)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1834.76(15)
Z	4
$\rho_{calc}g/cm^3$	1.373
μ/mm^{-1}	2.244
F(000)	800.0
Crystal size/mm^3	0.25 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.772 to 54.996
Index ranges	$-10 \leq h \leq 10, -11 \leq k \leq 11, -33 \leq l \leq 33$
Reflections collected	37018
Independent reflections	4211 [$R_{int} = 0.0499$, $R_{sigma} = 0.0305$]
Data/restraints/parameters	4211/0/211
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	$R_1 = 0.0178$, $wR_2 = 0.0432$
Final R indexes [all data]	$R_1 = 0.0217$, $wR_2 = 0.0437$
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.34
Flack parameter	0.014(3)

Table S14. Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for Substrate (Eq 6). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br01	2873.2(3)	5669.1(2)	3912.8(2)	28.31(6)
O002	8717.5(18)	2250.2(16)	8237.1(6)	31.7(3)
C003	6019.1(19)	4977.8(19)	6132.5(7)	16.1(3)
C004	8859(2)	4720(2)	5713.6(8)	20.9(4)
C005	5895(2)	4900(2)	7129.5(8)	18.8(4)
C006	8578.1(19)	4342(2)	6674.0(7)	16.6(3)
C007	6244(2)	4752.5(19)	5161.3(8)	19.1(4)
C008	7730(2)	4141.5(18)	6151.6(7)	16.7(3)
C009	4036(2)	5884(2)	4588.6(7)	21.1(4)
C00A	7928(2)	4846.8(19)	5212.0(7)	21.0(4)
C00B	7456.4(19)	3901.4(19)	7136.7(7)	16.1(4)
C00C	5037(2)	4654(2)	5625.4(7)	16.5(4)
C00D	8734(2)	4156(2)	7592.5(7)	18.2(4)
C00E	6935(2)	2267.2(19)	7122.4(8)	19.8(4)
C00F	5425(2)	4726(2)	4632.2(8)	24.3(4)
C00G	2742(2)	5762(2)	5023.1(7)	22.7(4)
C00H	3657(2)	5853(2)	5543.2(7)	20.9(4)
C00I	4916(2)	4733(2)	6619.7(7)	19.0(4)
C00J	4197(2)	3111(2)	5632.4(8)	22.6(4)
C00K	8186(2)	3436(2)	8094.3(8)	22.5(4)
C00L	10456(2)	3602(2)	7373.0(8)	21.8(4)
C00M	10266(2)	3548(2)	6779.2(8)	21.7(4)
C00N	6861(3)	4245(3)	8408.8(8)	36.1(5)

Table S15. Anisotropic displacement parameters ($Å^2×10^3$) for Substrate (Eq 6). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br01	32.93(10)	26.75(10)	25.26(10)	-0.08(8)	-4.07(9)	0.64(9)
O002	26.0(7)	25.2(8)	43.8(10)	11.8(7)	-1.6(7)	1.2(7)
C003	10.5(7)	13.3(8)	24.3(10)	0.5(7)	4.0(7)	2.3(6)
C004	12.0(7)	19.2(10)	31.4(11)	4.3(7)	7.7(7)	2.2(7)
C005	13.1(7)	20.6(9)	22.6(10)	-1.2(7)	3.7(7)	4.6(7)
C006	9.9(6)	11.1(7)	28.7(10)	1.2(8)	3.9(6)	-0.2(8)
C007	18.8(8)	14.3(9)	24.1(11)	1.3(7)	6.1(8)	3.0(8)
C008	11.0(6)	13.6(8)	25.5(9)	0.8(7)	4.9(7)	0.0(7)
C009	22.1(8)	18.8(10)	22.5(10)	0.9(7)	-0.8(7)	-1.1(8)
C00A	19.2(8)	17.8(8)	26(1)	3.3(7)	8.9(8)	2.5(9)
C00B	11.3(8)	12.3(8)	24.6(10)	0.0(6)	1.4(6)	0.3(6)
C00C	12.9(7)	14.2(9)	22.3(10)	0.0(6)	4.6(7)	0.0(7)
C00D	13.4(7)	12.2(9)	29.1(10)	-1.0(7)	-1.0(7)	1.0(7)
C00E	17.0(8)	15.0(8)	27.4(10)	1.8(7)	3.2(7)	-3.4(8)
C00F	24.3(9)	23.6(11)	25.1(11)	0.6(7)	6.8(8)	3.4(8)
C00G	17.3(7)	24.7(9)	26.1(9)	-1.7(8)	-0.5(7)	2.9(10)
C00H	15.3(7)	23.3(10)	24(1)	-2.7(8)	1.8(7)	4.5(8)
C00I	11.2(7)	22.6(10)	23.2(11)	0.6(7)	4.0(7)	3.0(7)
C00J	21.9(9)	18.8(10)	27.3(12)	0.1(7)	1.2(7)	-5.3(8)
C00K	16.1(8)	21.5(9)	29.8(11)	0.3(7)	-4.4(7)	-0.7(8)
C00L	11.6(7)	17.7(9)	36.2(12)	-1.0(8)	-1.2(7)	1.0(7)
C00M	10.6(7)	20.2(10)	34.3(12)	1.9(8)	2.5(7)	1.5(7)
C00N	38.9(11)	46.1(13)	23.5(11)	2.9(10)	0.7(8)	14.7(12)

Table S16. Bond lengths for Substrate (Eq 6).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br01	C009	1.9784(19)	C007	C00C	1.531(2)
O002	C00K	1.209(2)	C007	C00F	1.510(3)
C003	C008	1.544(2)	C009	C00F	1.517(2)
C003	C00C	1.547(3)	C009	C00G	1.518(3)
C003	C00I	1.543(2)	C00B	C00D	1.564(2)
C004	C008	1.529(2)	C00B	C00E	1.534(2)
C004	C00A	1.491(3)	C00C	C00H	1.549(2)
C005	C00B	1.524(2)	C00C	C00J	1.543(3)
C005	C00I	1.531(3)	C00D	C00K	1.512(3)
C006	C008	1.515(2)	C00D	C00L	1.550(2)
C006	C00B	1.537(2)	C00G	C00H	1.525(2)
C006	C00M	1.533(2)	C00K	C00N	1.509(3)
C007	C00A	1.333(2)	C00L	C00M	1.540(3)

Table S17. Bond angles for Substrate (Eq 6).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C008	C003	C00C	111.66(14)	C006	C00B	C00D	100.22(13)
C00I	C003	C008	113.14(15)	C00E	C00B	C006	112.61(15)
C00I	C003	C00C	112.41(13)	C00E	C00B	C00D	109.36(14)
C00A	C004	C008	112.52(15)	C007	C00C	C003	109.94(14)
C00B	C005	C00I	110.89(15)	C007	C00C	C00H	106.63(15)
C008	C006	C00B	114.07(13)	C007	C00C	C00J	109.08(15)
C008	C006	C00M	118.82(15)	C00H	C00C	C003	109.44(14)
C00M	C006	C00B	103.74(15)	C00J	C00C	C003	112.01(15)
C00A	C007	C00C	122.87(19)	C00J	C00C	C00H	109.60(14)
C00A	C007	C00F	120.88(18)	C00K	C00D	C00B	113.42(14)
C00F	C007	C00C	116.25(16)	C00K	C00D	C00L	115.01(15)
C004	C008	C003	108.31(14)	C00L	C00D	C00B	103.79(15)
C006	C008	C003	110.68(14)	C007	C00F	C009	111.28(16)
C006	C008	C004	111.19(14)	C009	C00G	C00H	109.28(15)
C00F	C009	Br01	109.27(13)	C00G	C00H	C00C	114.40(15)
C00G	C009	Br01	109.54(12)	C005	C00I	C003	113.79(14)
C00G	C009	C00F	112.18(16)	O002	C00K	C00D	122.99(18)
C007	C00A	C004	124.59(18)	O002	C00K	C00N	120.3(2)
C005	C00B	C006	107.39(14)	C00N	C00K	C00D	116.66(17)
C005	C00B	C00D	116.06(15)	C00M	C00L	C00D	106.83(14)
C005	C00B	C00E	110.82(14)	C006	C00M	C00L	104.16(15)

IX. Actinometry

Determination of light intensity. All actinometric experiments were conducted in a Luzchem photoreactor equipped with 350 nm lamps. The light intensity was calibrated using ferrioxalate actinometer (4.0 mL volume in 10 mL quartz tubes), following the Hatchard-Parker method.[8] Solutions were irradiated for 0, 5, 10, 15, 20, 30, 35, 45 seconds, and the light intensity was determined for each run. The average photon flux was 7.8 x 10^{-8} einsteins s^{-1}.

Determination of the quantum yield. A 10 mL quartz test tube was charged with 4.0 mL of the standard reaction mixture, using CuBr (10 mg, 0.070 mmol), ligand **L1** (3.8 mg, 0.0070 mmol), LiO*t*-Bu (168 mg, 2.1 mmol), $BocNH_2$ (246 mg, 2.1 mmol), and 2-bromo-4-phenylbutane (149 mg, 0.70 mmol) in DME (8 mL). The test tube was capped with a rubber septum, placed in the Luzchem photoreactor, and irradiated with 350 nm lamps for 30 or 60 min. Next, a 20 mL vial was charged with a measured quantity of an internal standard (1,3,5-trimethoxybenzene). The unpurified reaction mixture was then added to the 20 mL vial that contained the internal standard, ensuring quantitative transfer through EtOAc rinses (2 mL x 3). An aliquot was concentrated in vacuo, and $CDCl_3$ was added. Then, the solids were removed by filtration through a piece of cotton, and the filtrate was subjected to analysis via ^{1}H NMR spectroscopy. The reported quantum yield of 0.06 is the average of three runs (0.061, 0.063, and 0.056).

Determination of the lifetime of copper complex 1. A Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series; 355 nm) was used as the source of the excitation pulse in the Beckman Institute Laser Resource Center (BILRC; California Institute of Technology). Transmitted light from the sample was detected with a photomultiplier tube (Hamamatsu R928). All instruments and electronics in these systems were controlled by software written in LabVIEW (National Instruments).

Figure S22. Representative fitting of the luminescence decay of copper complex **1** at 427 nm.

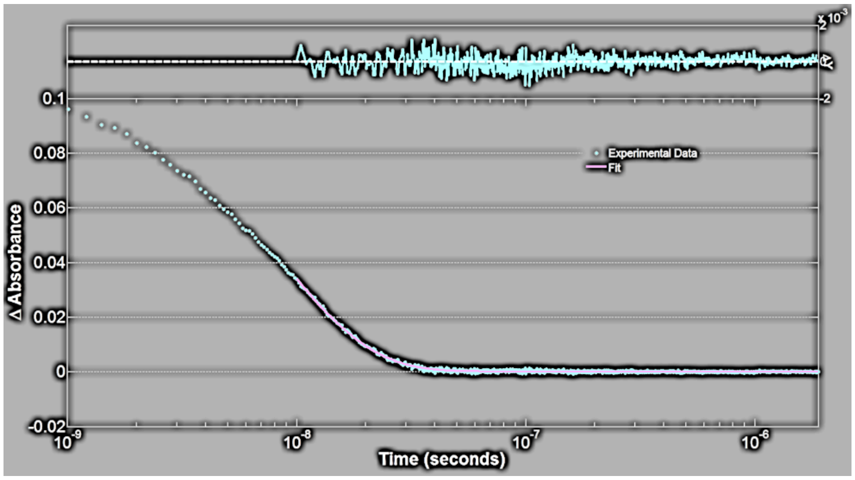


Table S18. Luminescence lifetimes of copper complex **1** at various emission wavelengths in THF.

Entry	Emission wavelength	Lifetime	Average lifetime
1	427 nm	7.87 ns	8.12 ns
2	432 nm	7.92 ns	
3	455 nm	8.39 ns	
4	405 nm	8.25 ns	
5	415 nm	8.08 ns	

Note on the chain length.[9] Under the simplest scenario, the quenching fraction, Q, of the standard reaction is determined by:

$$Q = \frac{k[RBr]}{\tau_o^{-1} + k[RBr]} = \frac{(1.7{\times}10^9\ s^{-1}M^{-1})(0.088\ M)}{(8.1{\times}10^{-9}\ s)^{-1} + (1.7{\times}10^9\ s^{-1}M^{-1})(0.088\ M)} = 0.55$$

where τ_o is the lifetime of copper complex **1**, and $k = K_{SV}/\tau_o$ is the quenching rate coefficient of 2-bromo-4-phenylbutane, and $[RBr]$ is the concentration of 2-bromo-4-phenylbutane. This represents the maximum quenching fraction, which gives a minimum for the chain length:

$$Minimum\ chain\ length = \frac{\Phi}{Q_{max}} = \frac{0.060}{0.55} = 0.11 < 1$$

If one takes into account the other potential quenching processes that may occur at a similarly fast rate, close to diffusion, under the standard conditions (e.g., any other material present in the standard reaction, including nucleophile, other Cu complexes, base, etc.), the quenching fraction, and thus the chain length, can be calculated:

$$Q = \frac{k[RBr]}{\tau_o^{-1} + k([RBr] + [Others])}$$

$$Q = \frac{(1.7{\times}10^9\ s^{-1}M^{-1})(0.088\ M)}{(8.1{\times}10^{-9}\ s)^{-1} + (1.7{\times}10^9\ s^{-1}M^{-1})(0.088\ M + 0.053\ M)} = 0.13$$

$$Chain\ length = \frac{0.060}{0.13} = 0.47 < 1$$

Even under this limiting scenario, the chain length remains less than unity, which is not suggestive of a chain process.

References

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(6) Lusztyuk, J.; Maillard, B.; Deycard, S.; Lindsay, D. A.; Ingold, K. U. *J. Org. Chem.* **1987**, *52*, 3509–3514.

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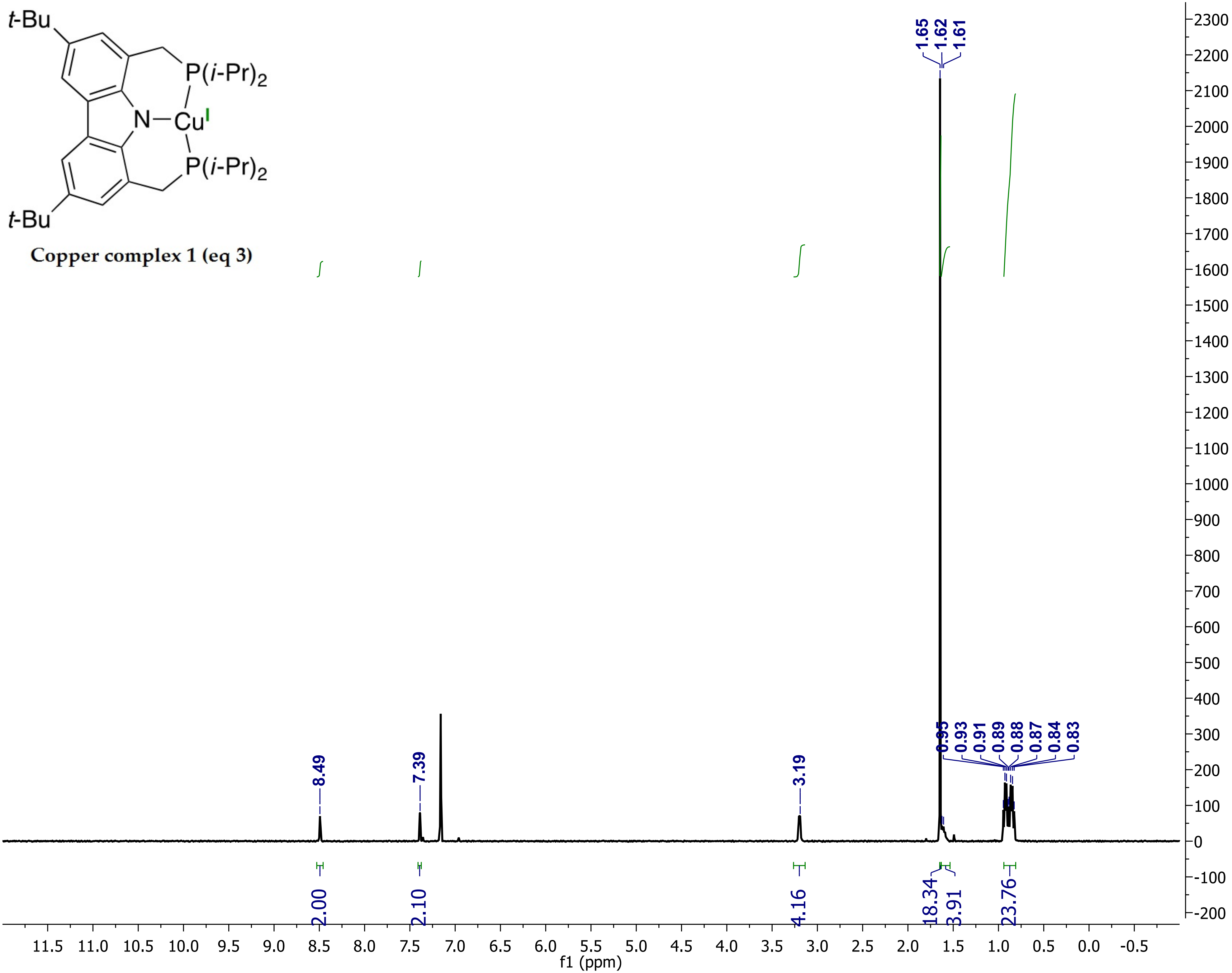
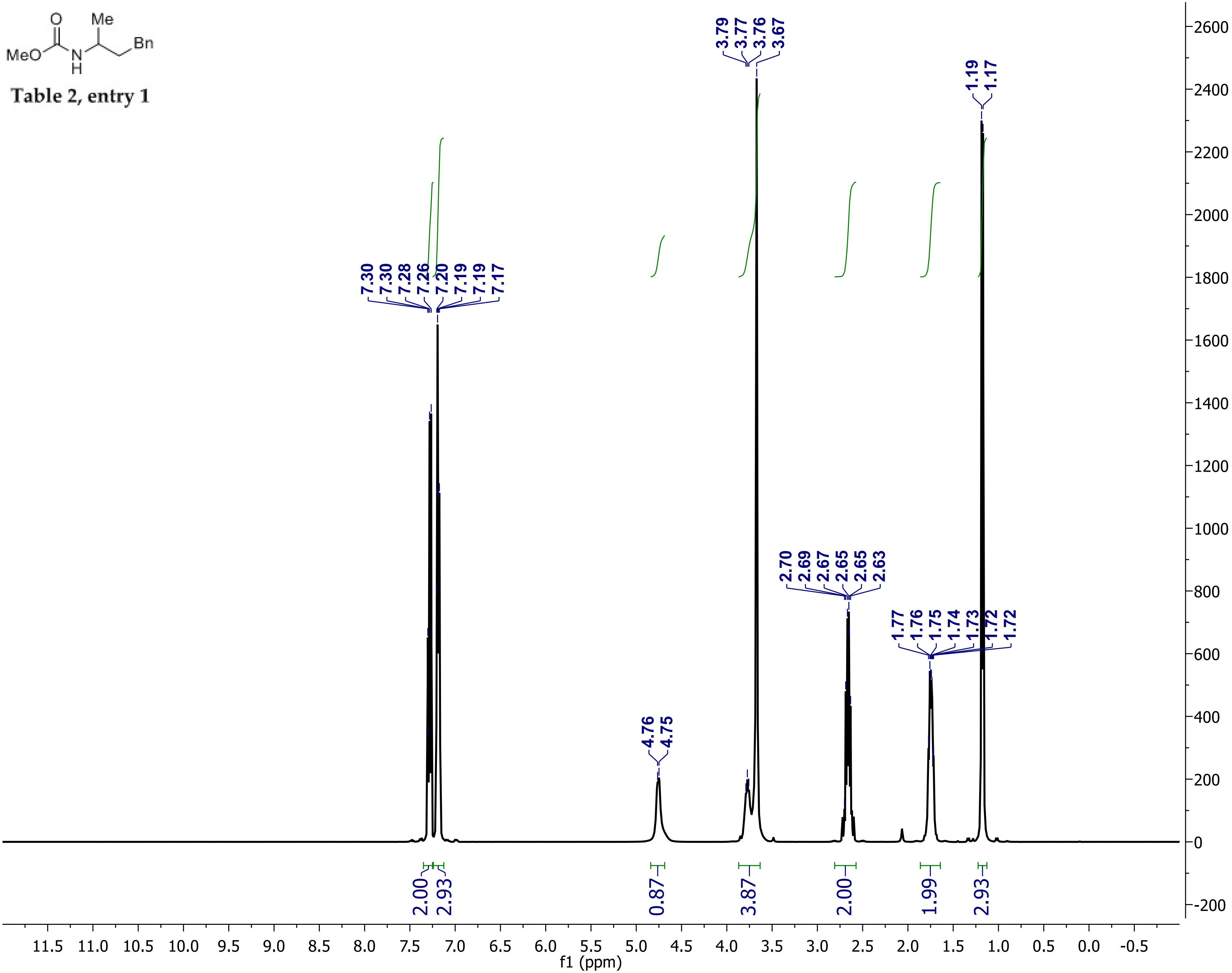
X. NMR Spectra



Copper complex 1 (eq 3)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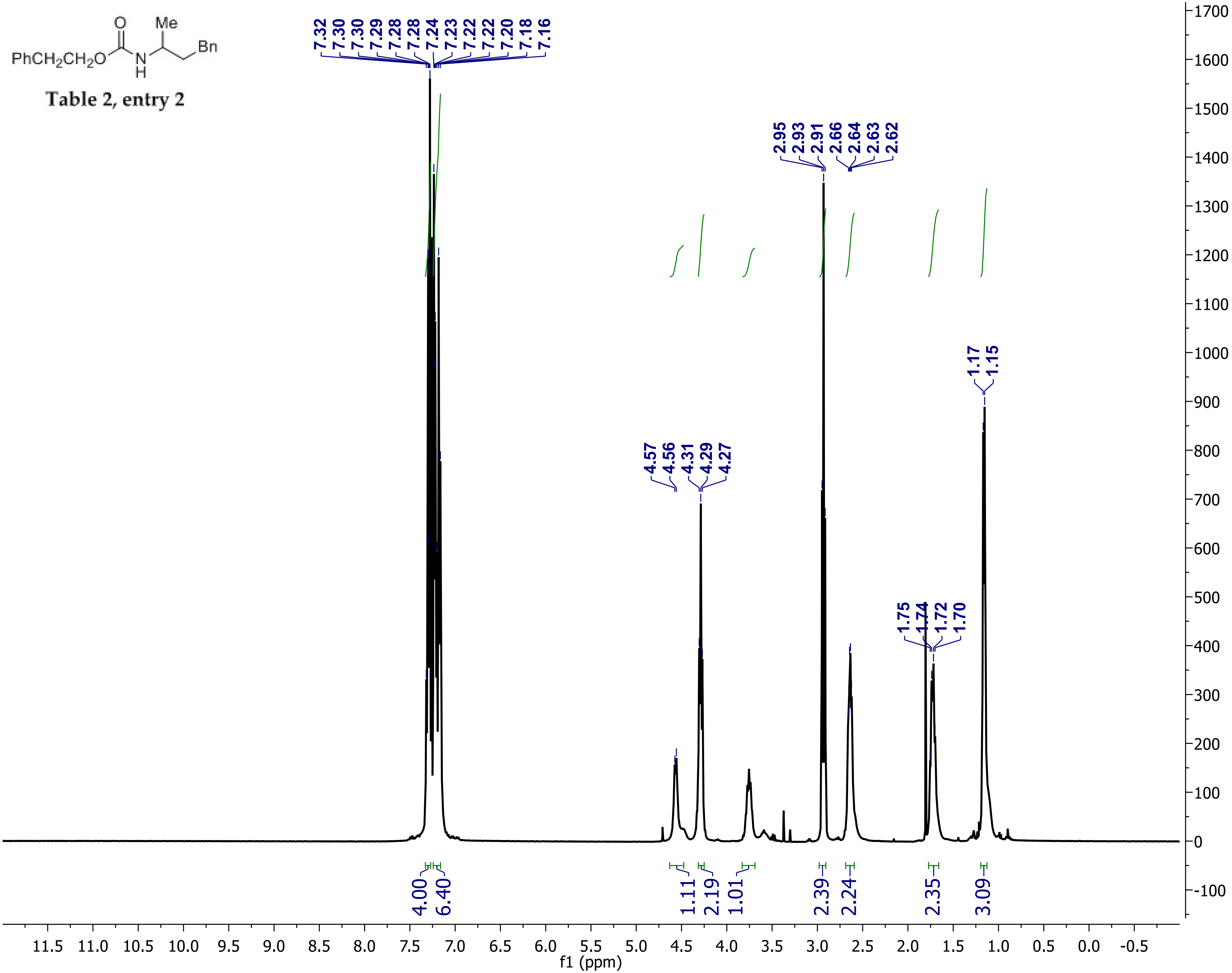

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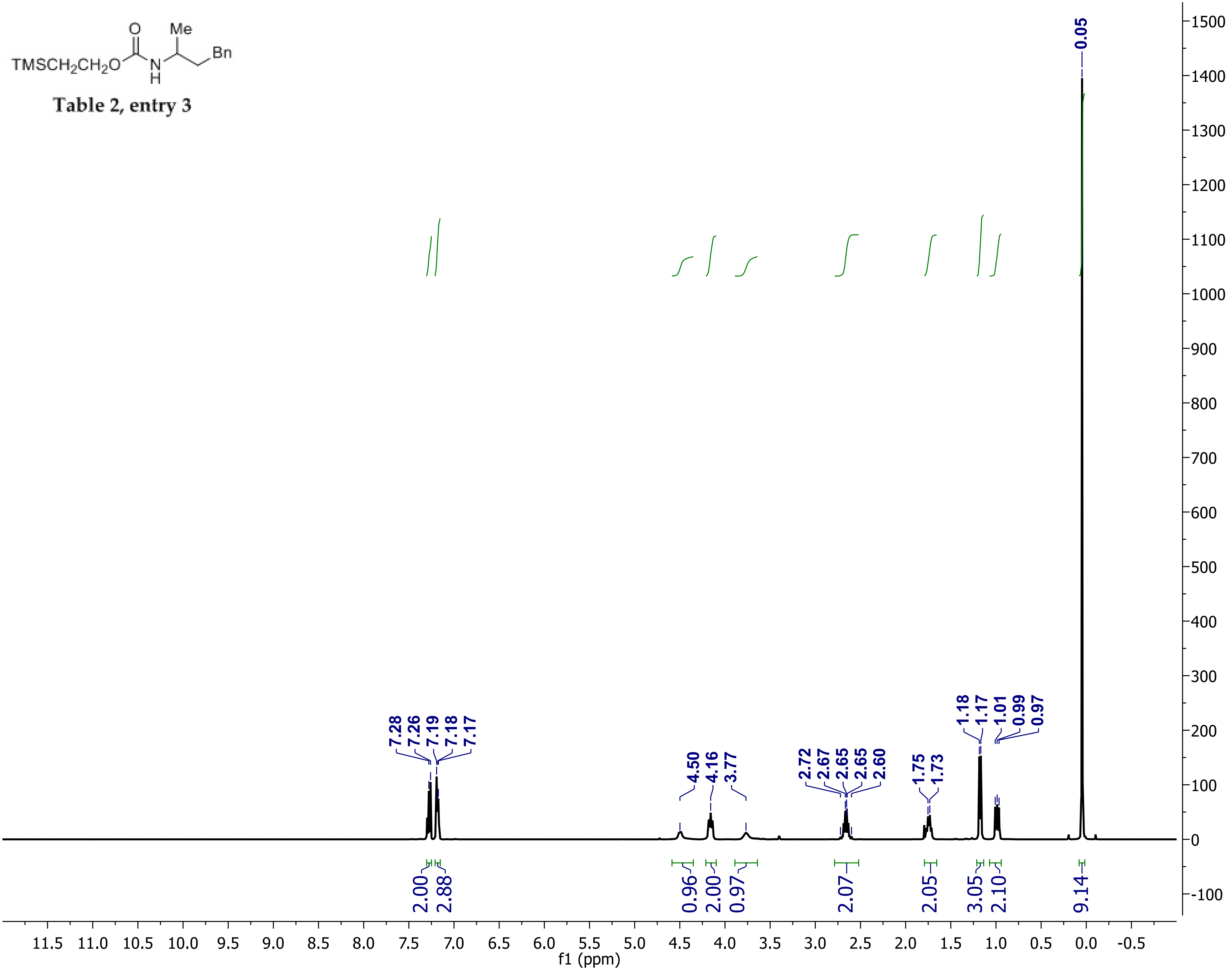

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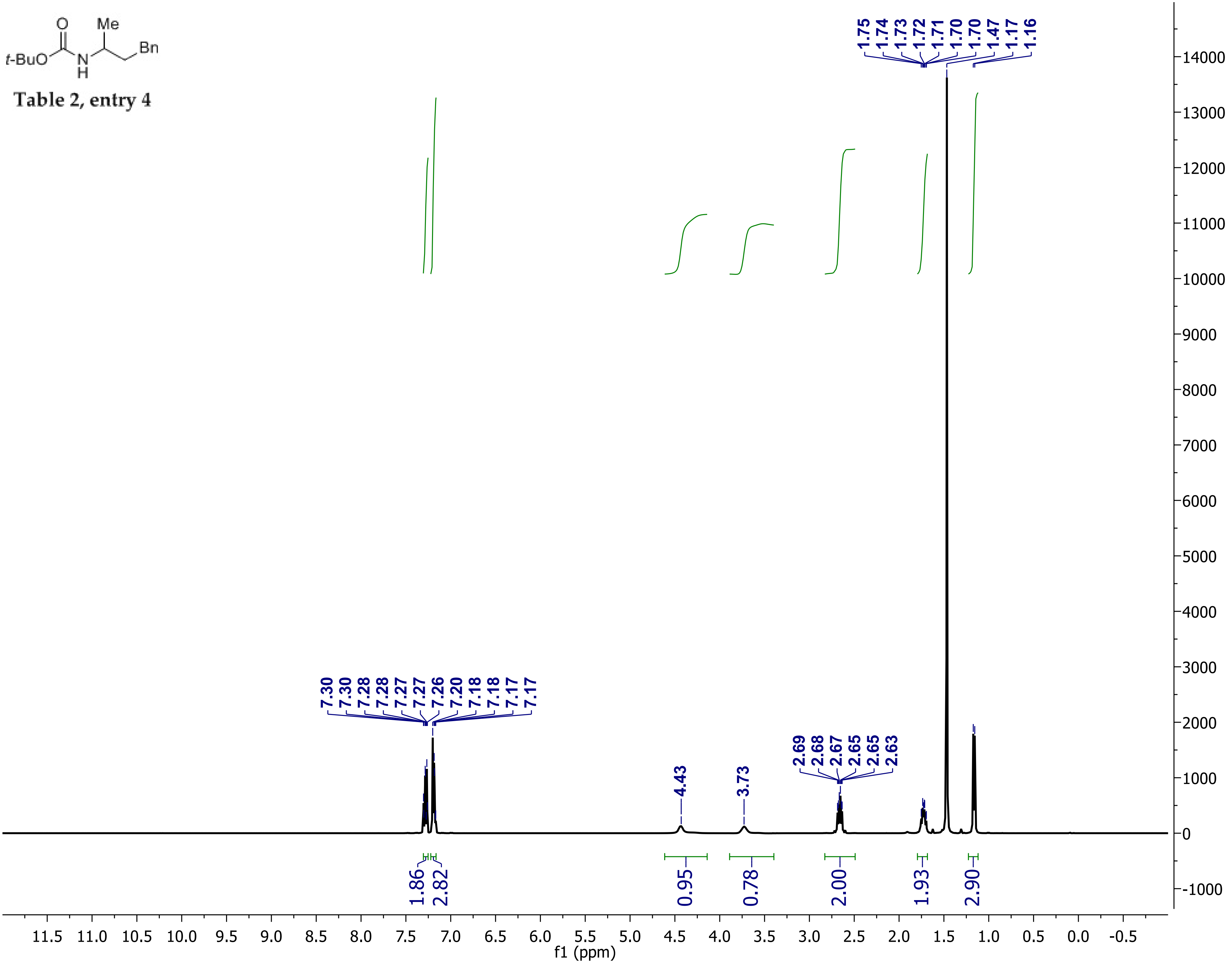

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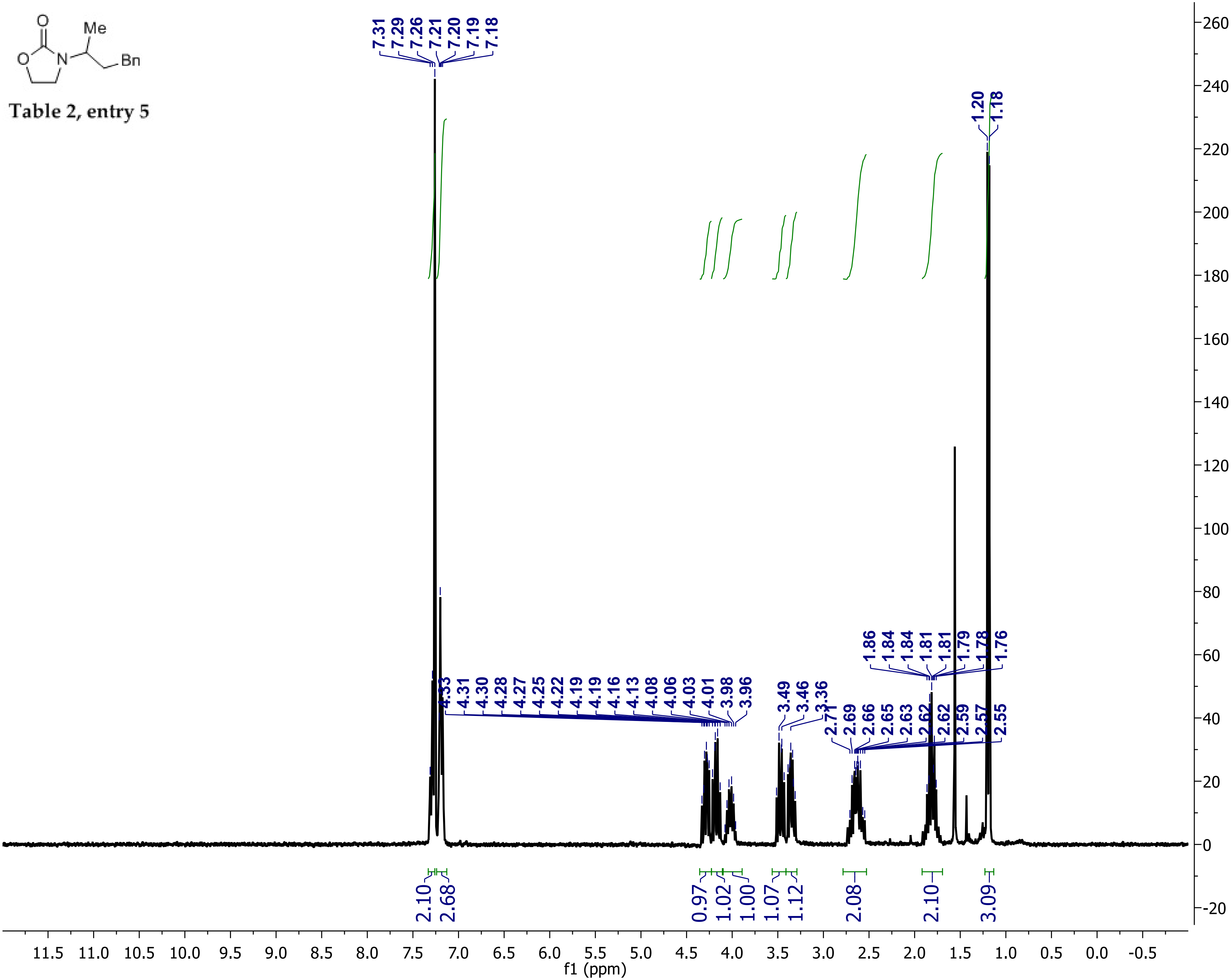
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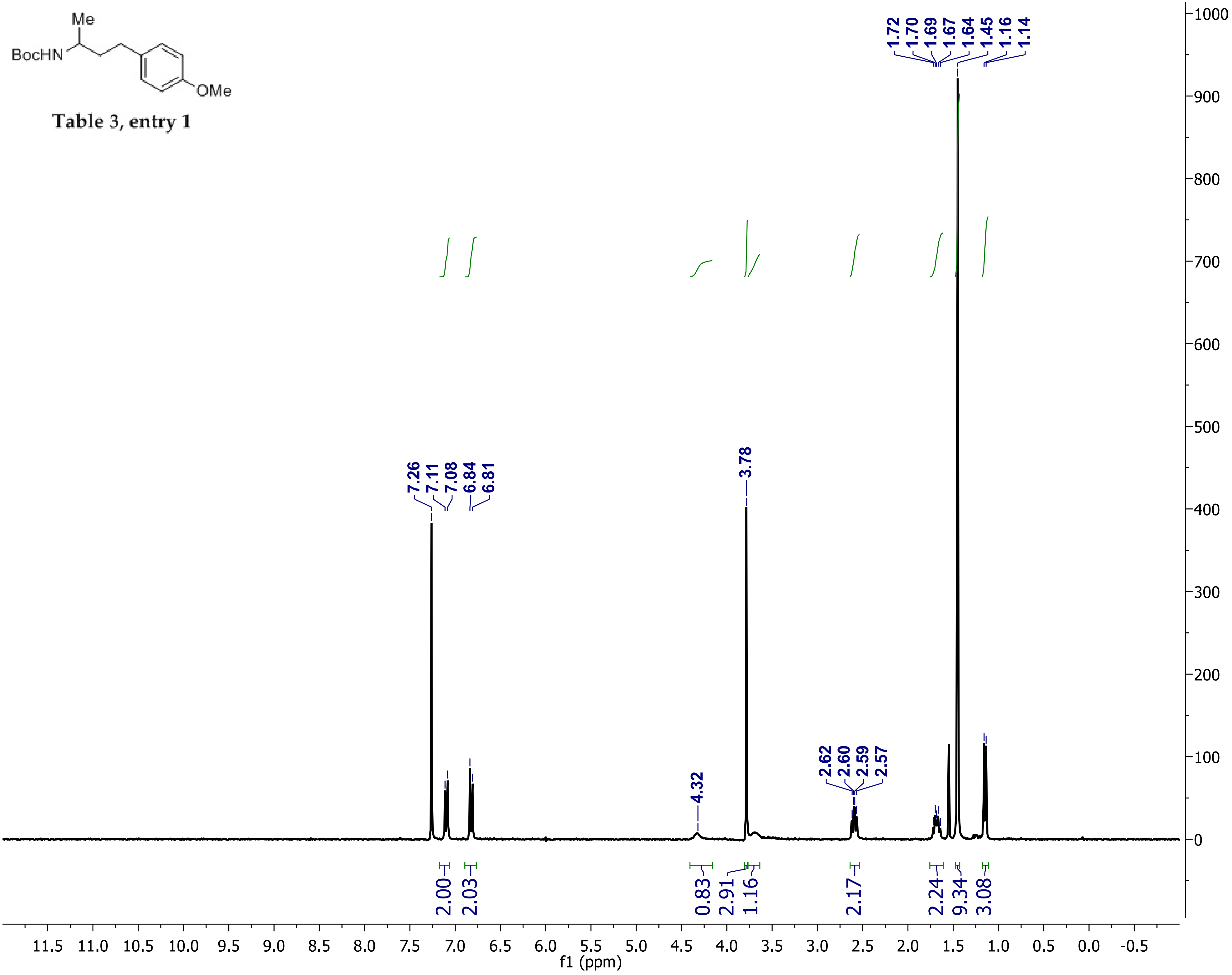
Me
BocHN
OMe
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7.11
7.08
6.84
6.81
4.32
3.78
2.62
2.60
2.59
2.57
1.72
1.70
1.69
1.67
1.64
1.45
1.16
1.14
2.00
2.03
0.83
2.91
1.16
2.17
2.24
9.34
3.08
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
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900
800
700
600
500
400
300
200
100
0

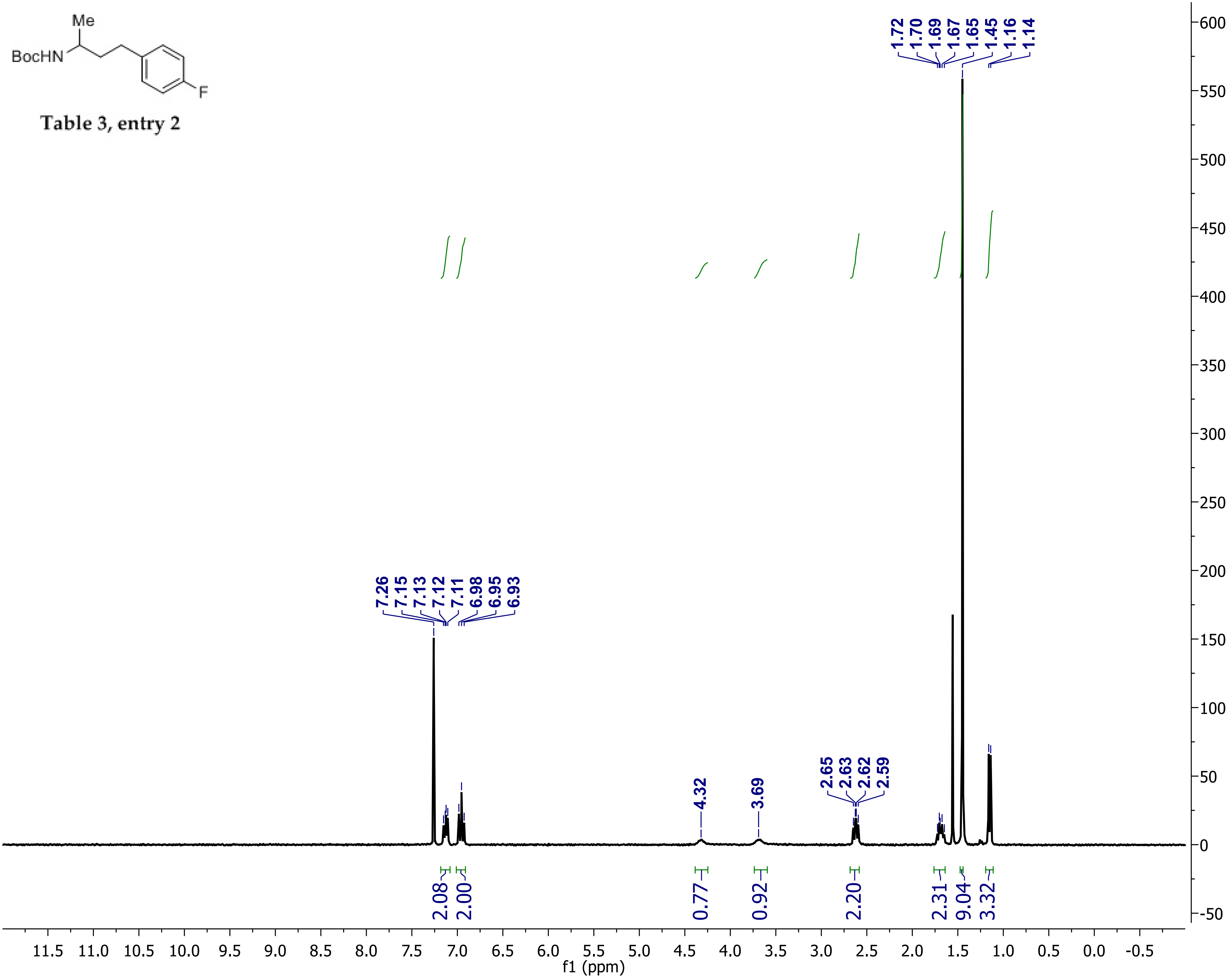
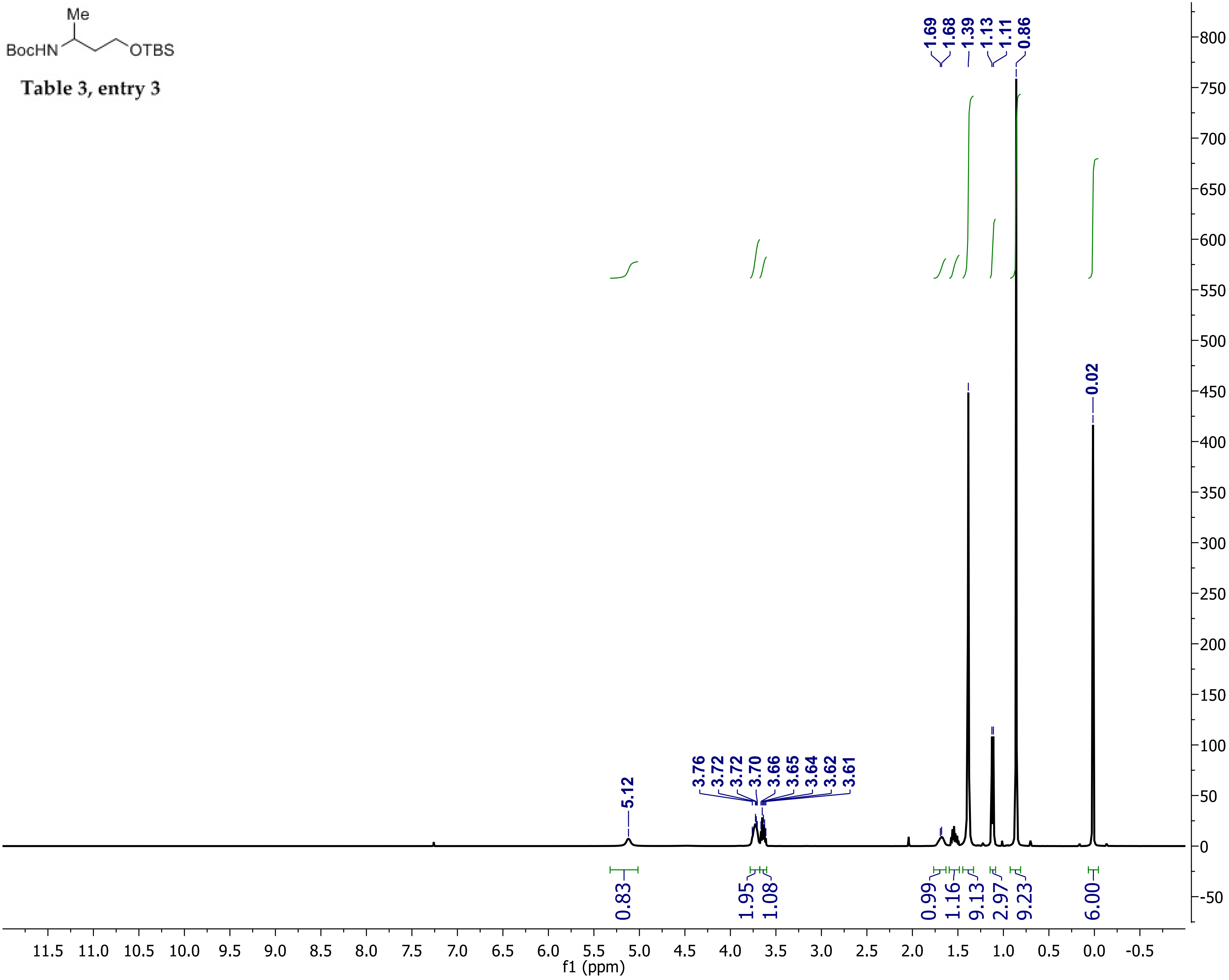


Table 3, entry 2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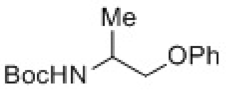

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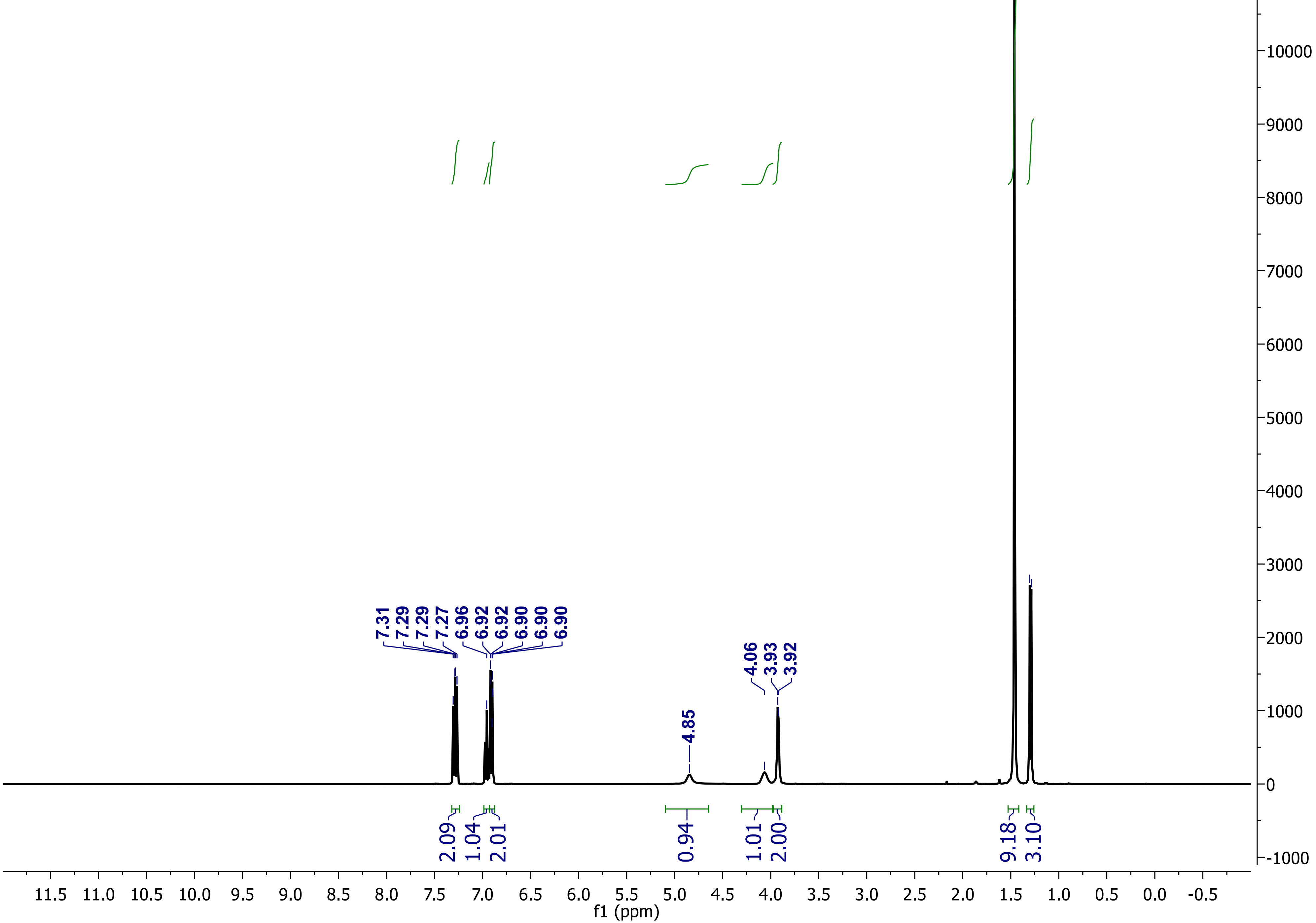

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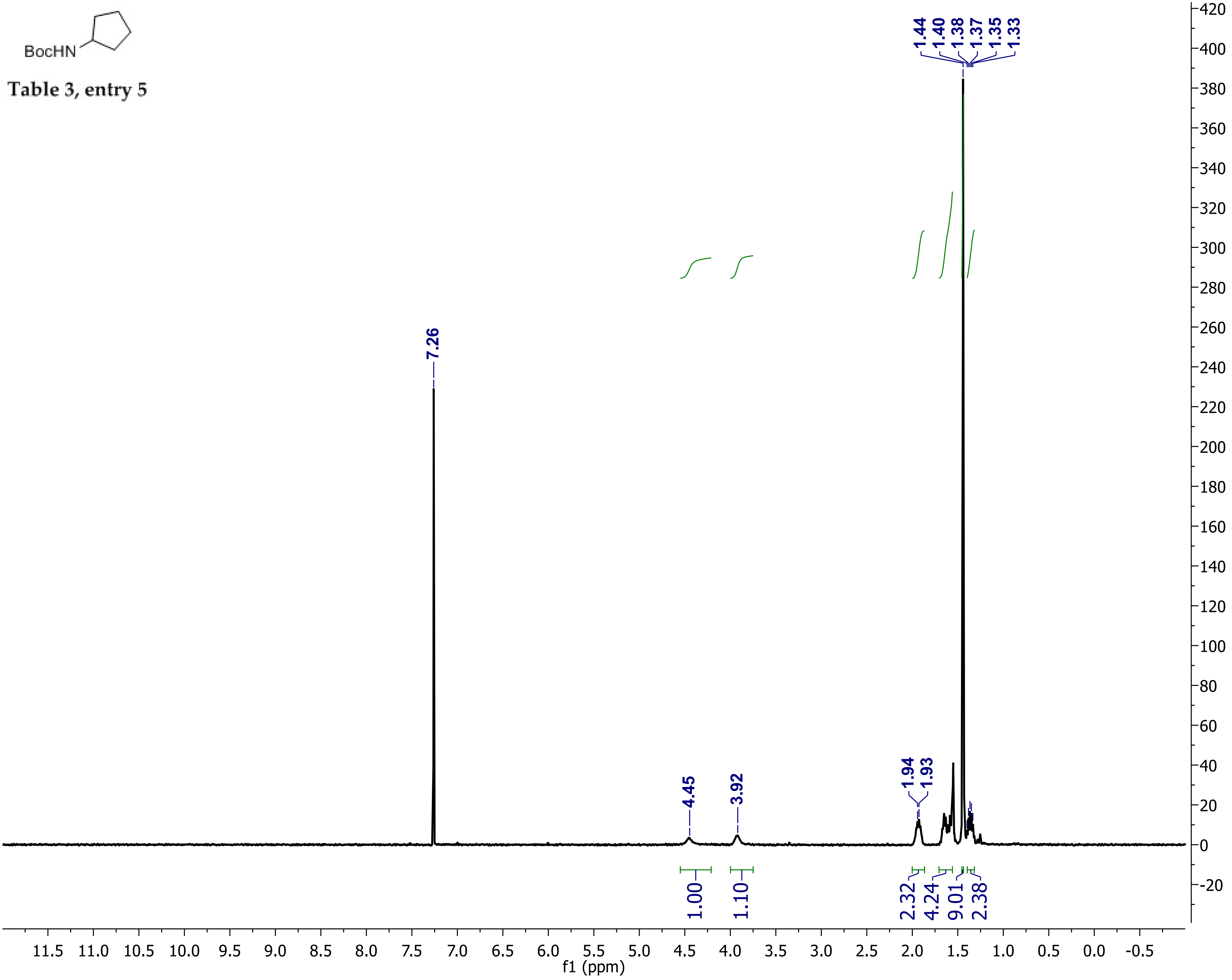

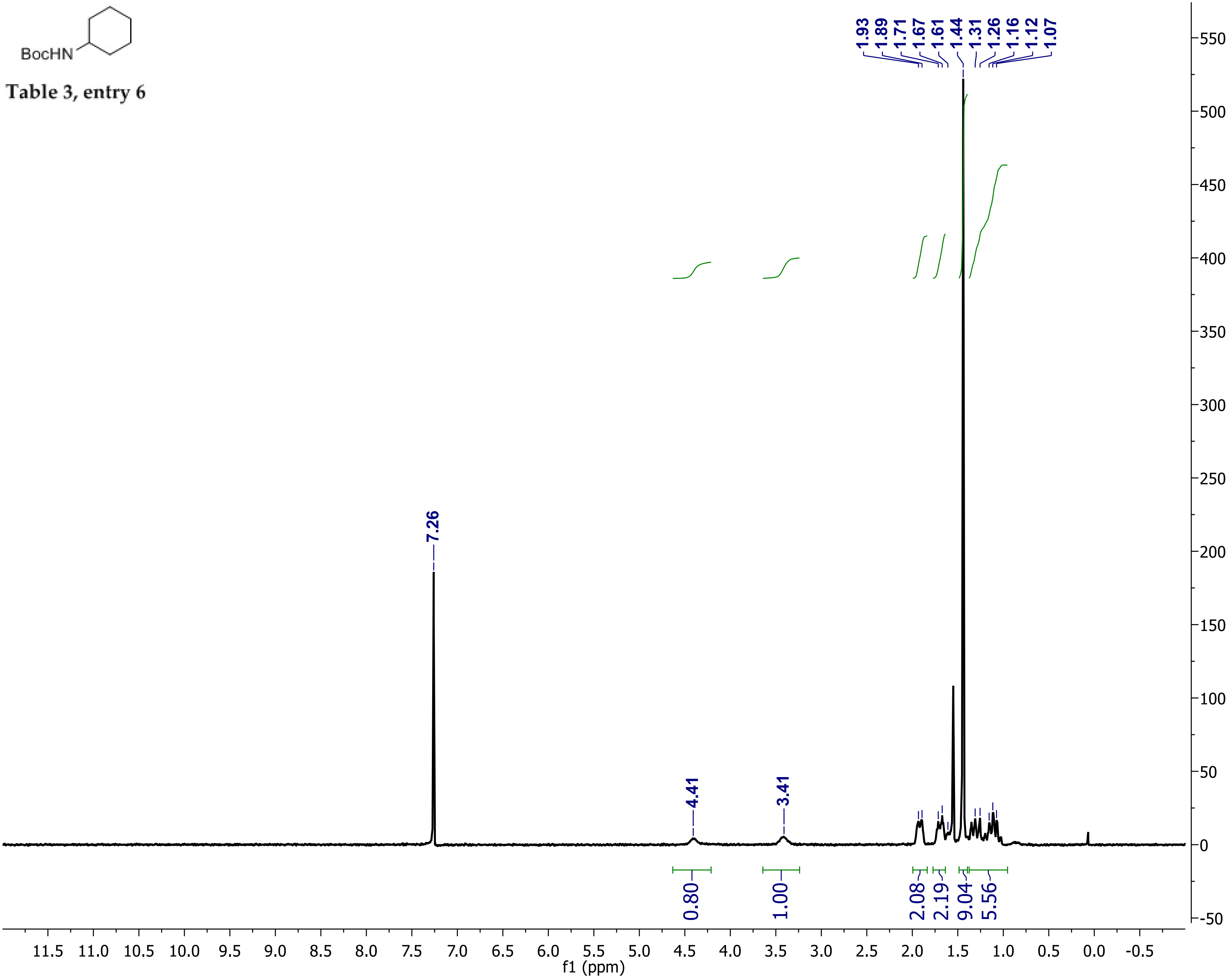

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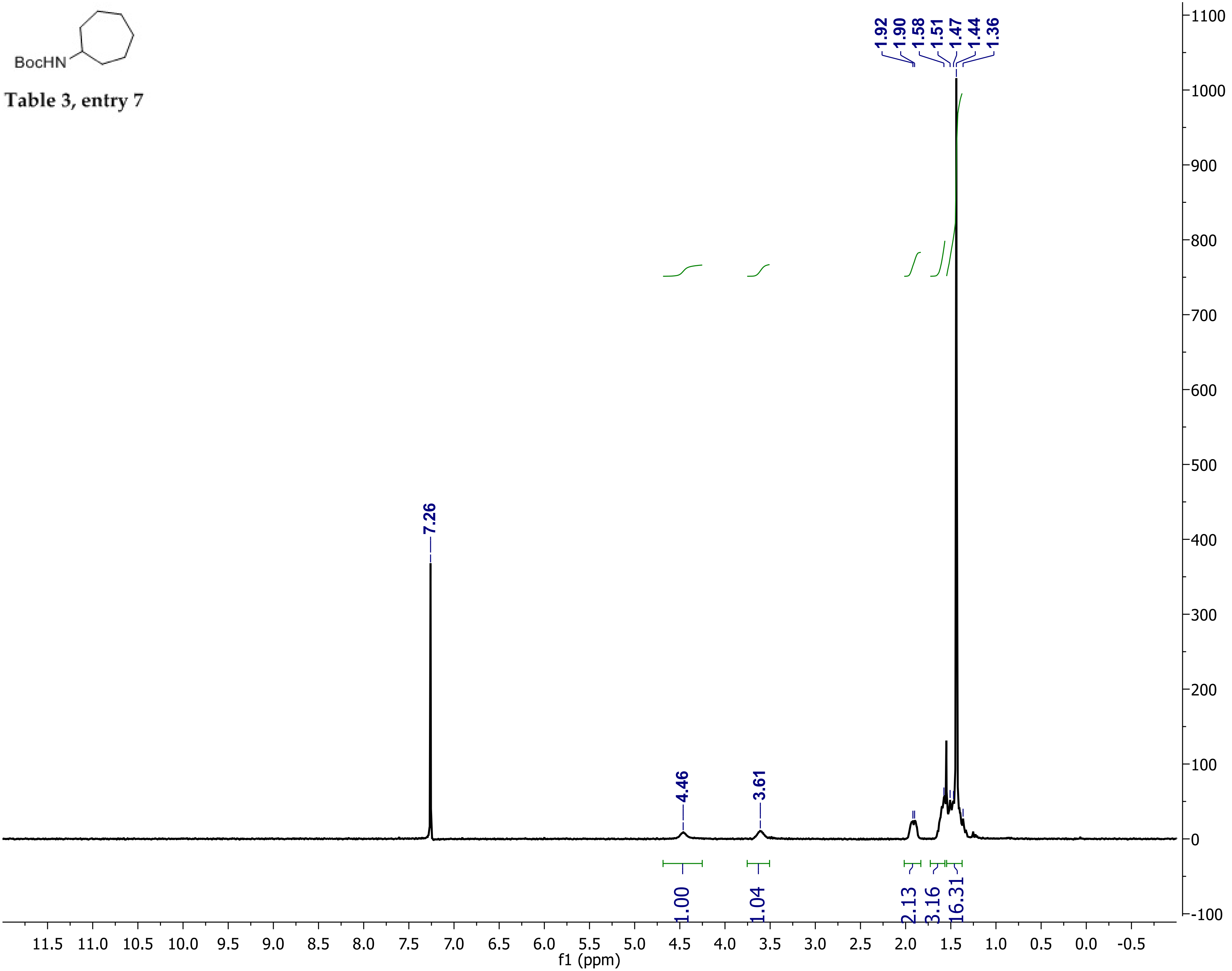

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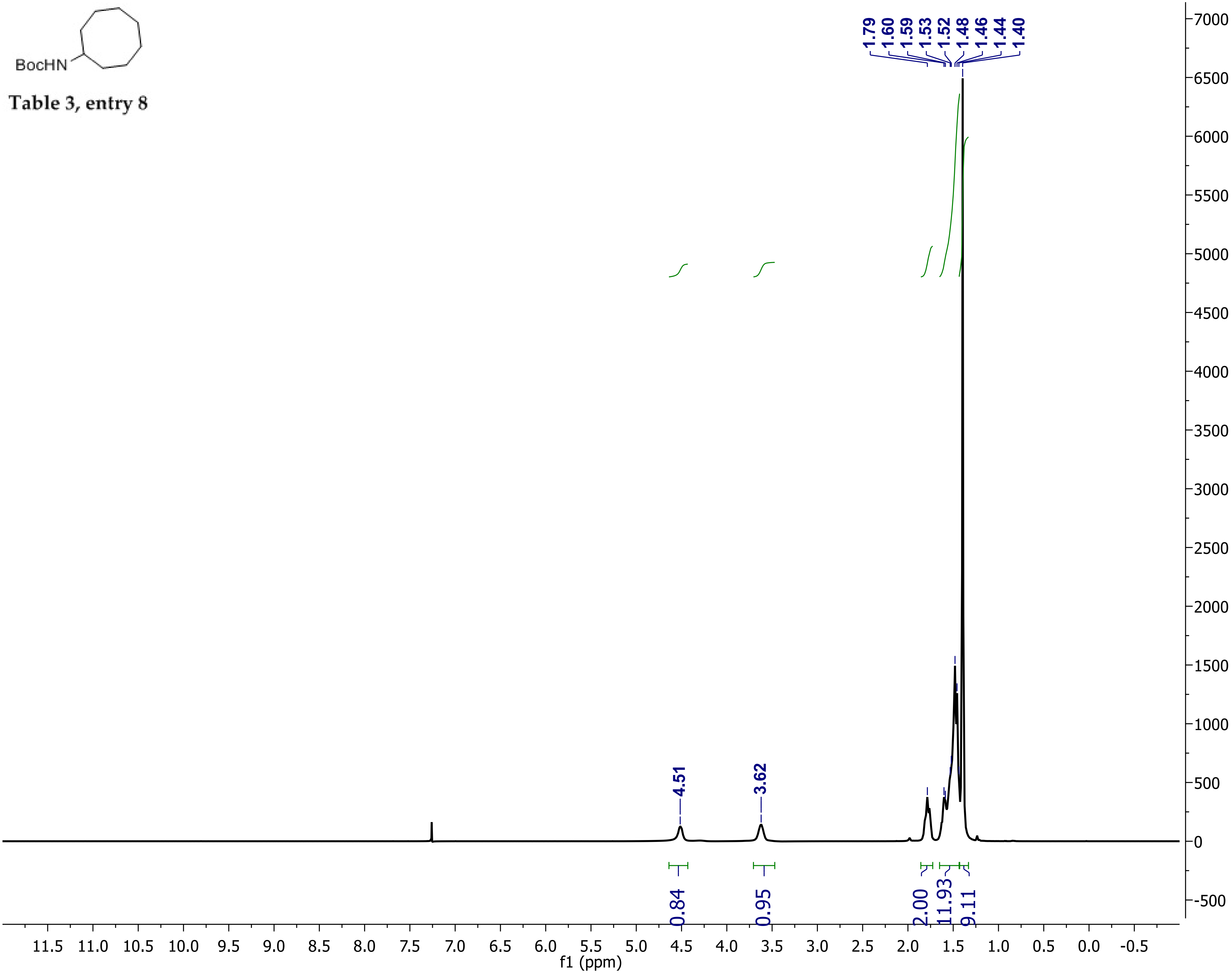
BocHN
Table 3, entry 8
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1.59
1.53
1.52
1.48
1.46
1.44
1.40
4.51
3.62
0.84
0.95
2.00
11.93
9.11
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

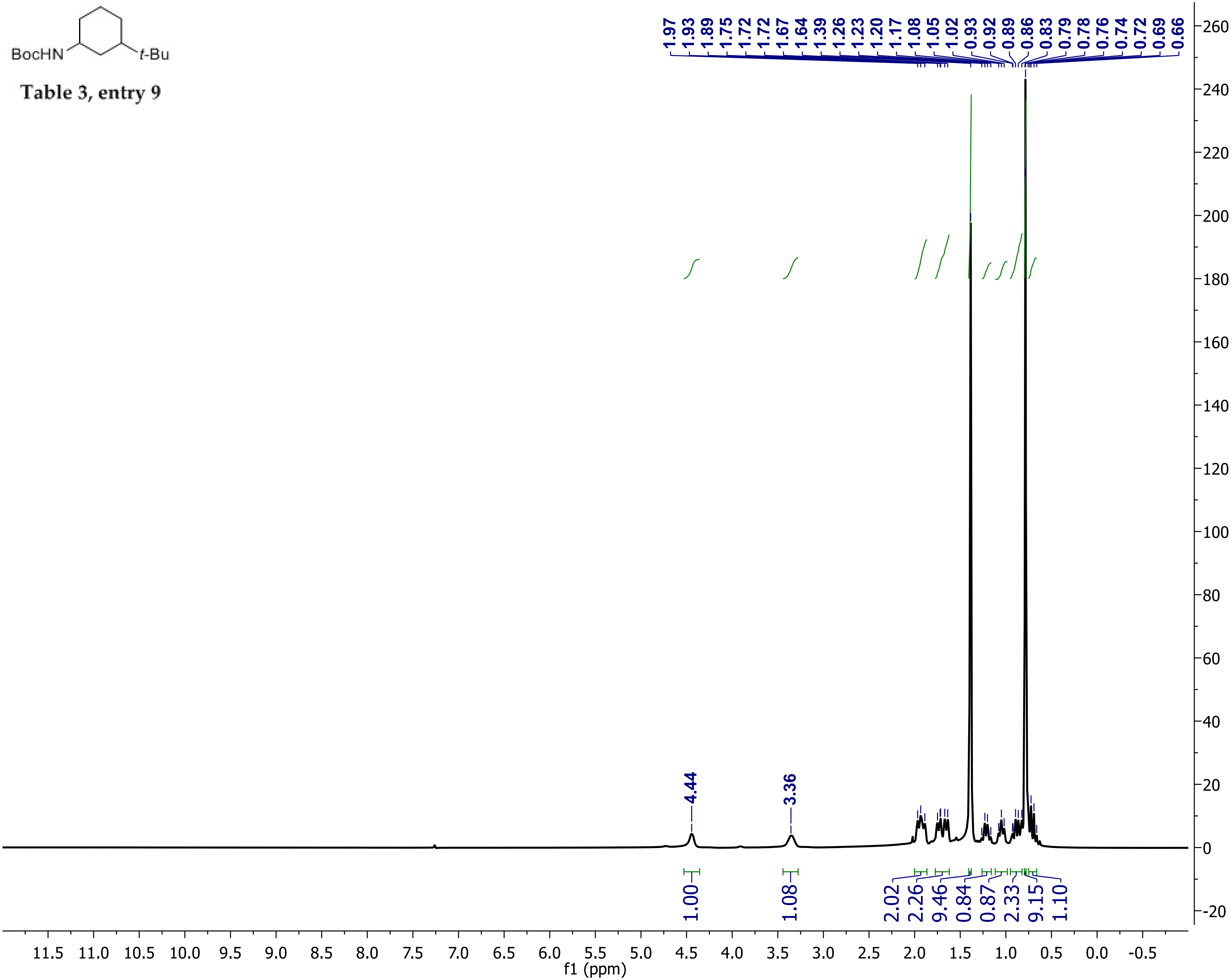
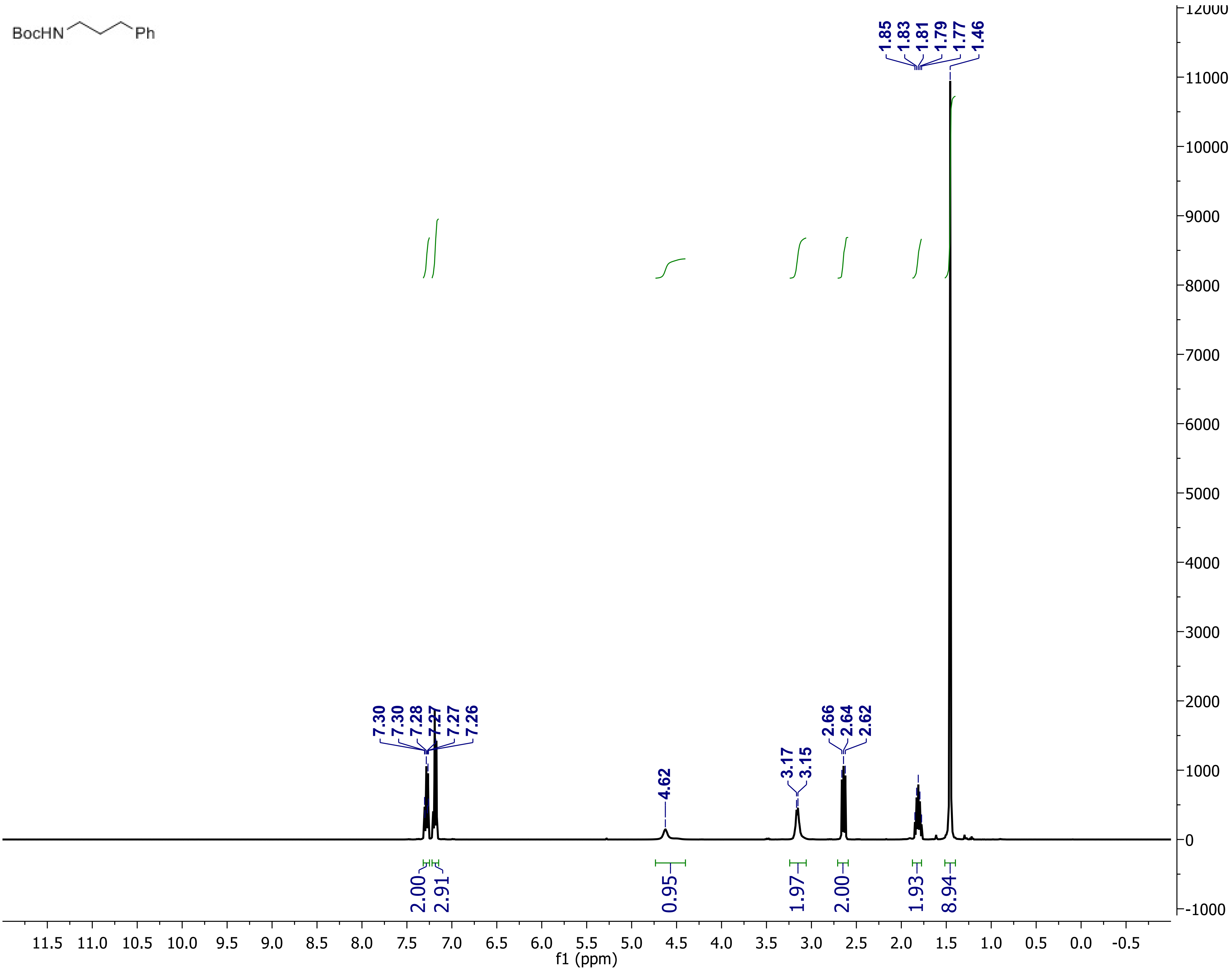


Table 3, entry 9


BocHN
Ph
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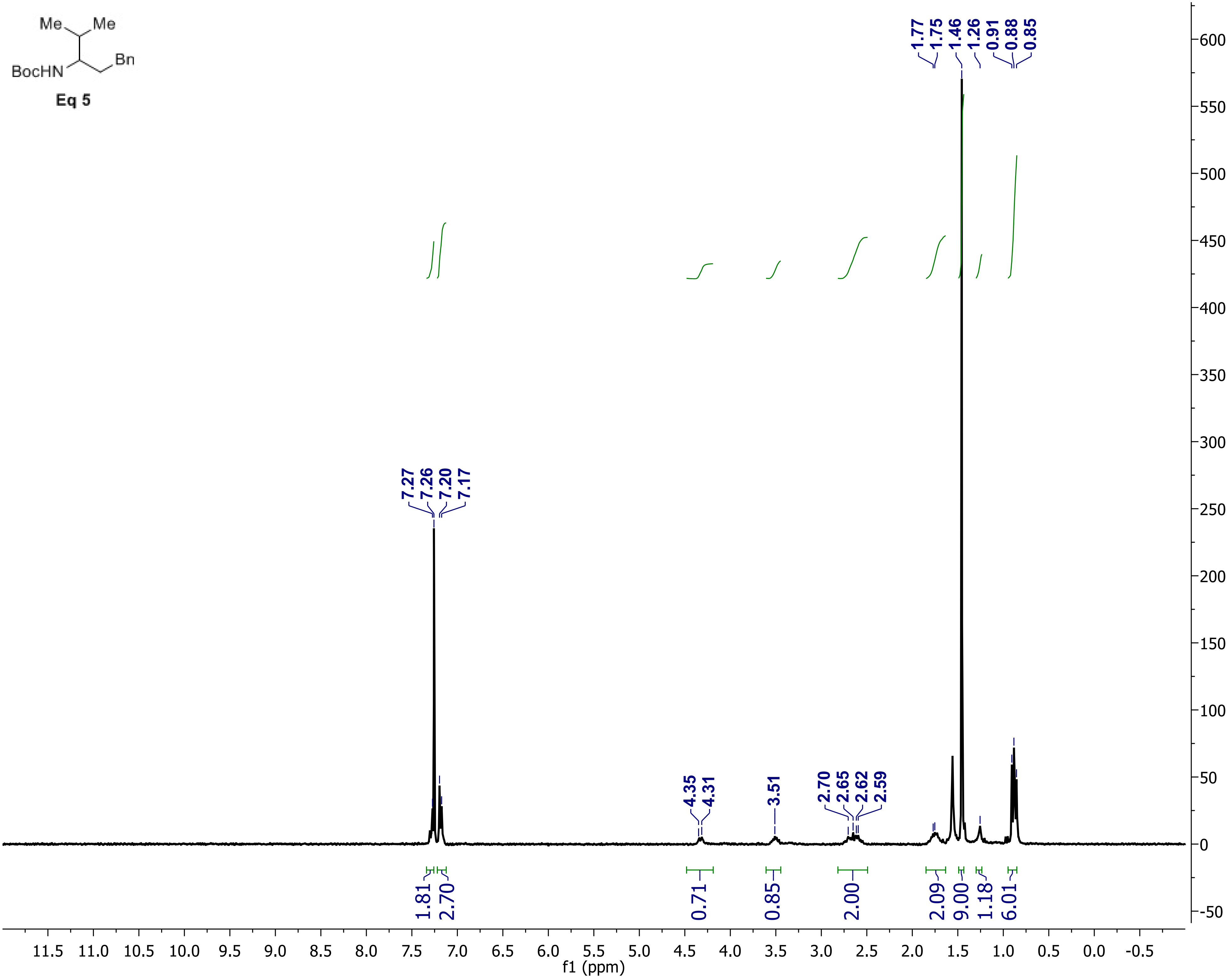
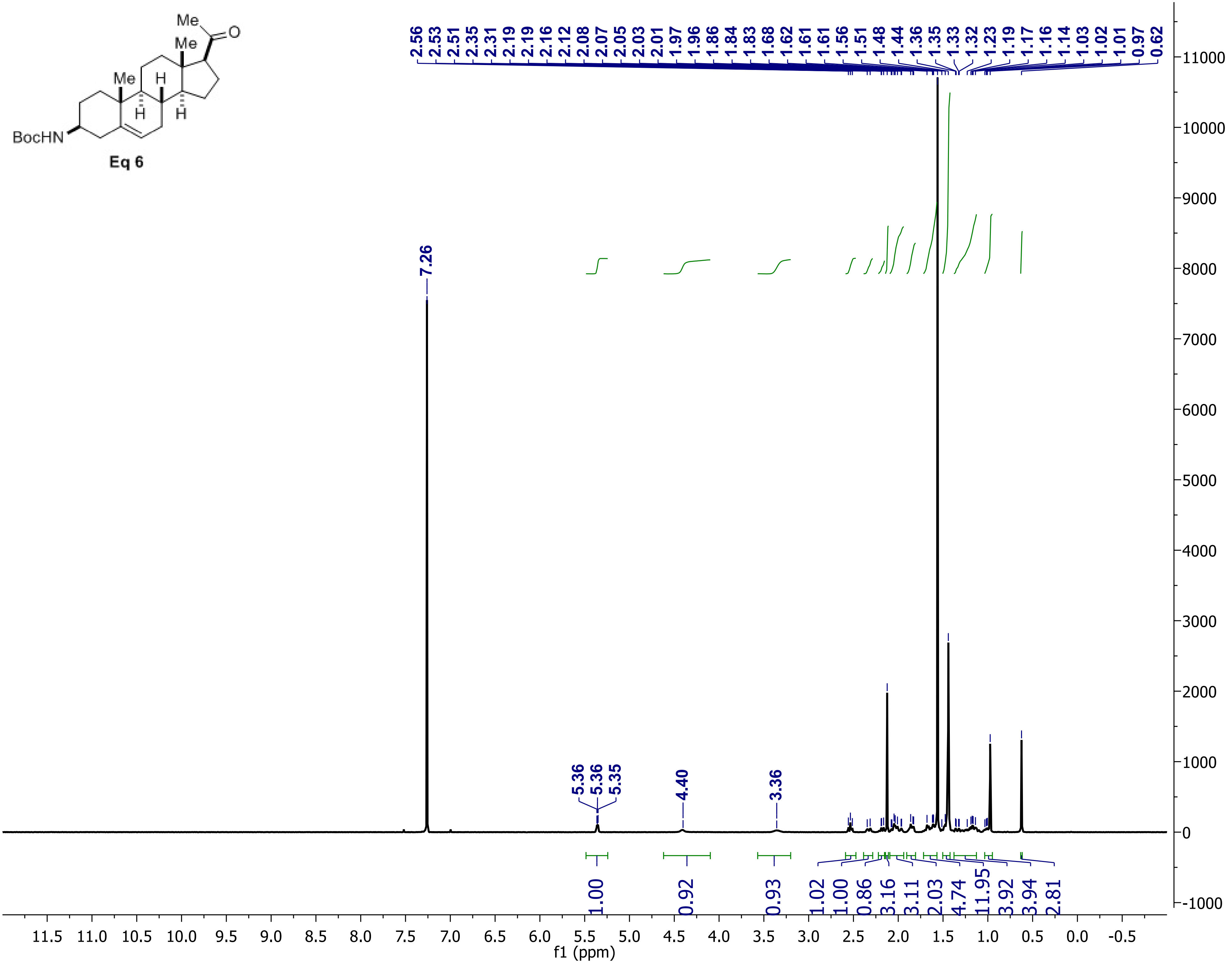
1.79
1.77
1.46
7.30
7.30
7.28
7.27
7.27
7.26
4.62
3.17
3.15
2.66
2.64
2.62
2.00
2.91
0.95
1.97
2.00
1.93
8.94
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Me
Me
BocHN
Bn
Eq 5
1.77
1.75
1.46
1.26
0.91
0.88
0.85
7.27
7.26
7.20
7.17
4.35
4.31
3.51
2.70
2.65
2.62
2.59
1.81
2.70
0.71
0.85
2.00
2.09
9.00
1.18
6.01
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



Eq 6

Me
Me
Me
H
H
H
O
BocHN
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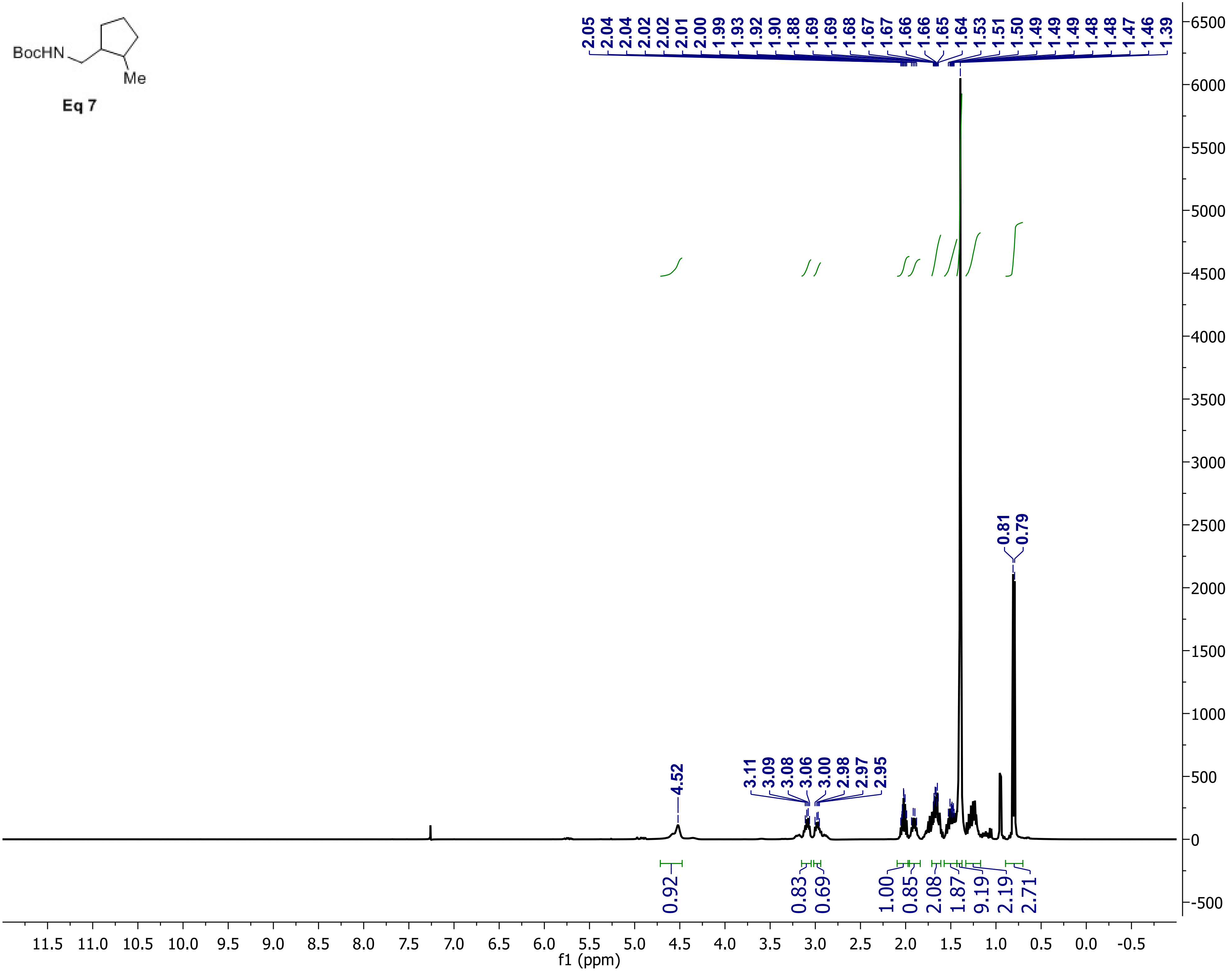
7.26
5.36 5.36 5.35
4.40
3.36
1.00
0.92
0.93
1.02 1.00 0.86 3.16 3.11 2.03 4.74 11.95 3.92 3.94 2.81
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


BocHN
Me
2.05
2.04
2.04
2.02
2.02
2.01
2.00
1.99
1.93
1.92
1.90
1.88
1.69
1.69
1.68
1.67
1.67
1.66
1.66
1.65
1.64
1.53
1.51
1.50
1.49
1.49
1.49
1.48
1.48
1.47
1.46
1.39
0.81
0.79
4.52
3.11
3.09
3.08
3.06
3.00
2.98
2.97
2.95
0.92
0.83
0.69
1.00
0.85
2.08
1.87
9.19
2.19
2.71
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

Eq 7